

however, is that the simple argument based on CFSE values gives an impressively good account of the thermodynamic data. Thus, while granting, freely, the point that CFSE values make up only a tiny fraction of the total enthalpies of forming complex ions from the gaseous metal ion and ligands, and cannot therefore be taken as useful measures of the absolute stability of complexes, the relative CFSE values in properly chosen homologous series of compounds appear capable, *in themselves*, of providing a semiquantitative guide to the relative stabilities of the members of the series. An early and now classic example of this sort of use of CFSE values is the correlation of the site preferences of various metal ions in mixed oxides (*e.g.*, spinels).^{15,16} The present results for process 9, which is not unrelated to the site preference problem, strongly support the fundamental validity of the theory proposed for the latter.

(15) D. S. McClure, *J. Phys. Chem. Solids*, **3**, 311 (1957).

(16) J. D. Dunitz and L. E. Orgel, *ibid.*, **3**, 318 (1957).

Finally, the results reported here permit us to evaluate a suggestion made by Gill and Nyholm^{2c} that there would be a difference in the mean slopes of the curves for H_{com} of octahedral and tetrahedral complexes sufficient to play an important role in the energetics of process 9. Figure 2 shows a plot similar to theirs except that we have used the actual rather than hypothetical results for the tetrahedral complexes. Qualitatively, the predicted effect is present: the gap between tetrahedral and octahedral curves closes by about 7 kcal./mole in going from Mn to Zn. However, this is too small an effect, only ~ 1 kcal./mole per element, to have any significant impact on the over-all results. The conclusion proposed above, *viz.*, that the CFSE values, *in themselves*, can pretty well account for the over-all thermochemical results, may thus be reiterated.

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A Molecular Orbital Treatment of the Bonding in Certain Metal Atom Clusters^{1a}

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The structures of the $[M_6X_8]^{4+}$, $M = \text{Mo, W (?)}$; $[M_6Cl_{12}]^{2+}$, $M = \text{Nb, Ta}$; and $[M_3X_{12}]^{3-}$, $M = \text{Re}$, species, which contain clusters of heavy transition metal atoms, are compared and the occurrence of approximately square MX_4 units is noted as a common feature. The metal-to-metal bonding within the clusters is treated by a simple molecular orbital method and it is shown that in this way all the general aspects of the electronic structures can be straightforwardly accounted for. Clues provided as to other possible metal ion cluster compounds are discussed.

Introduction

There exist three classes of compounds of the transition elements, aside from polynuclear metal carbonyls, in which the principal structural feature is a cluster of metal atoms in some symmetrical array at internuclear distances indicative of strong metal-metal interactions. These are (1) the $[M_6X_{12}]^{2+}$ systems in which M is Nb or Ta, (2) the $[M_6X_8]^{4+}$ systems in which M is Mo and, probably, though this is not entirely certain, W, and (3) the recently discovered $[\text{Re}_3\text{Cl}_{12}]^{3-}$ anion. The first two systems have been recognized for a long time and various attempts have been made to treat the bonding therein. Thus, for both the $[M_6Cl_8]^{4+}$ and the $[M_6Cl_{12}]^{2+}$ types, molecular orbital treatment has been carried so far as to produce some parametric equations for orbital energies.² On the other hand, it has also been proposed that in addition to the molybdenum-chlorine bonding in $[\text{Mo}_6\text{Cl}_8]^{4+}$, the Mo-Mo bonds be considered as discrete, two-center bonds, thus affording a valence bond formulation of the bonding in which the

molybdenum is considered to have a valence of six.³ This valence bond approach has been elaborated, leading to the suggestion that the molybdenum atoms use sets of square antiprismatic hybrid orbitals with the Mo-Cl bonds then being extraordinarily bent.⁴

The present attempt at a molecular orbital treatment, embracing all three types of compound, has been undertaken for several reasons.

(1) We believe that a valence bond approach, based on formation of two-center metal-metal bonds by use of certain limiting, generally quite symmetrical, hybridization schemes (or even more general, less symmetrical ones), is not a useful *general* approach, although it may be sufficient in some instances.⁵ In most cases, the $[\text{Mo}_6\text{Cl}_8]^{4+}$ ion as depicted in Fig. 4 of ref. 4 being a cogent example, one must use bonds which are so bent or so

(3) J. C. Sheldon, *J. Chem. Soc.*, 1007, 3106 (1960).

(4) R. J. Gillespie, "Advances in the Chemistry of the Coordination Compounds," S. Kirschner, Ed., The Macmillan Co., New York, N. Y., 1961, p. 34.

(5) For example, in $\text{Os}_3(\text{CO})_{12}$ and analogous molecules, one may assume approximate octahedral hybridization at each metal atom, so that each one forms four Os-C two-center bonds and two, somewhat bent, $\text{Os}_2\text{-Os}_2$ two-center bonds and thus account for the diamagnetism of such compounds in a satisfactorily facile manner.

(1) (a) Supported by the United States Atomic Energy Commission; (b) Fellow of the Alfred P. Sloan Foundation; (c) N.S.F. Predoctoral Fellow.

(2) L. D. Crossman, D. P. Olsen, and G. H. Duffey, *J. Chem. Phys.*, **38**, 73 (1963).

disproportionately concentrated in one region of space about the atom that the classic conceptual simplicity of the two-center bond is virtually lost in the very procrustean attempt to retain it.

(2) In the $[M_6Cl_{12}]^{2+}$ species, the formal oxidation number of the metal atoms is $2\frac{1}{3}$. Obviously this does not suggest that a description of the bonding as an elaboration of two-center, two-electron bonds is particularly apropos.

(3) In fact, if one attempts to treat the $[M_6Cl_{12}]^{2+}$ system in terms of two-center bonds, it is immediately obvious that it is an electron-deficient system, there being only 16 electrons available to form 12 metal-metal bonds (counting only the nearest neighbor or octahedron-edge type interactions). Although in the boron hydrides, use of low-order multicenter bonds (most generally three-center ones) is justifiable on the basis of the actual groupings of the atoms, there is no natural stopping point short of the entire octahedron in going from two-center to polycenter bonding in the $[M_6X_n]$ species.

(4) In the case of $[Re_3Cl_{12}]^{3-}$, we have been unable to devise any description of the bonding based on two-center electron-pair bonds which simultaneously is free of awkwardly bent bonds, avoids *ad hoc* assumptions as to orbital energies, and leads to a closed electron configuration in agreement with the diamagnetism of the molecule.

(5) As will be shown in the following section, there are certain notable similarities in the environments of the metal atoms in the $[M_6X_8]^{4+}$, $[M_6X_{12}]^{2+}$, and $[M_3X_{12}]^{3-}$ species and we believe that a proper description of the bonding should take explicit cognizance of this, as opposed to treating each as a separate case.

(6) The treatment of Crossman, Olsen, and Duffey does not lend itself to satisfying point 5 above, nor did it appear very tractable for computational purposes. It should be stressed that we have no criticism of Crossman, Olsen, and Duffey's work from an abstract point of view; to the extent that comparisons are possible, there is good agreement with our own work.

Comparison of Structures

Though there are some evident dissimilarities, the structures of the $[M_6X_8]^{4+}$, $[M_6Cl_{12}]^{2+}$, and $[M_3Cl_9]$ groups have several important structural features in common.

(i) In each of them, each metal atom lies at the center of an approximately square MX_4 group. These MX_4 groups are then combined in one of several ways which result in the sharing of X atoms between M atoms. It can be calculated from the published dimensions⁶ of the $[Nb_6Cl_{12}]^{2+}$, $[Ta_6Cl_{12}]^{2+}$, and $[Ta_6Br_{12}]^{2+}$ ions in alcohol solution that the angles between M-X bonds and the fourfold axes of the metal atom

octahedra are $\sim 81^\circ$. Thus, the "square" MX_4 groups are apparently slightly distorted in the sense of having the planes of X atoms a little outside the planes for perfectly square MX_4 units, although the extent of this apparent distortion is hardly, if at all, outside the limits of experimental error. In the $[Mo_6Cl_8]^{4+}$ ion,⁷ the $MoCl_4$ groups are planar to within the experimental uncertainties though these may be easily as large as ± 0.05 Å. in respect to chlorine atom positions. Finally, in the $[Re_3Cl_{12}]^{3-}$ structure⁸ there are $ReCl_4$ groups which are planar except for a distortion which seems largely, if not entirely, due to van der Waals repulsions between chlorine atoms on different rhenium atoms.

(ii) The combining of the square MX_4 units, with formation of M_2X and M_3X bridging arrangements, also involves the formation of clusters of metal atoms within which the metal-metal interactions appear to be quite strong judging from the shortness of the metal-metal distances. In $[Re_3Cl_{12}]^{3-}$ the Re-Re distances⁸ are 2.48 ± 0.01 Å., in $[Mo_6Cl_8]^{4+}$ the Mo-Mo distances across octahedral edges are 2.64 ± 0.05 Å., in $[Nb_6Cl_{12}]^{2+}$ the shortest Nb-Nb distances are ~ 2.85 Å., and in $[Ta_6Cl_{12}]^{2+}$ and $[Ta_6Br_{12}]^{2+}$ the Ta-Ta distances are ~ 2.90 Å.

(iii) In each case, the group formed by the cluster of metal atoms and those halogen atoms which have been regarded as belonging to the square MX_4 units shows affinity for additional ligands, evidently in such a way that each metal atom can bond one additional ligand using a centrifugally directed orbital. Thus, in $[Re_3Cl_{12}]^{3-}$, the most tightly bound grouping appears to be $[Re_3Cl_9]$ (Re-Cl distances of 2.36–2.39 Å.), with an additional chloride ion attached to each rhenium atom more loosely (Re-Cl distances of 2.52 Å.). Sheldon⁹ has shown that the $[Mo_6Cl_8]^{4+}$ entity persists through many chemical processes, exchanging its chlorine atoms with chloride ions in aqueous or moist ethanolic media immeasurably slowly, while forming numerous species of the type $[(Mo_6Cl_8)X_6]^{2-}$ or $[(Mo_6Cl_8)L_2X_4]$ where X represents a monodentate anion (e.g., Cl^- , OH^-) and L, a neutral monodentate ligand, such as an amine, alcohol, or H_2O . The presence of these six additional groups is indicated by Brosset's X-ray studies. In $[(Mo_6Cl_8)(OH)_4(H_2O)_2] \cdot 12H_2O$ there appears to be an oxygen atom ~ 2.3 Å. from each molybdenum atom,^{7a} while in $[(Mo_6Cl_8)Cl_4(H_2O)_8] \cdot 6H_2O$ four of the molybdenum atoms bind chlorine atoms and the other two oxygen atoms^{7b} with the Mo-Cl distances being given as 2.43 Å. The molybdenum to bridging chlorine atom distances reported for the $[Mo_6Cl_8]^{4+}$ group in $[(Mo_6Cl_8)(OH)_4(H_2O)_2] \cdot 12H_2O$ are 2.5–2.6 Å.; thus, the "additional" chlorine atoms are apparently more closely bound than those belonging to the $(Mo_6Cl_8)^{4+}$ group, contrary to the results for $[(Re_3Cl_9)Cl_3]^{3-}$. In view of Sheldon's results, as well as the comparison with the rhenium compound, a more

(6) P. A. Vaughan, J. H. Sturtevant, and L. Pauling, *J. Am. Chem. Soc.*, **72**, 5477 (1950). It should be noted that the structures are derived from analysis of the diffuse scattering of X-rays by solutions of the complex ions, rather than by X-ray crystallographic techniques; thus the uncertainties in metal-halogen distances are difficult to assess objectively, but are almost certainly in excess of 0.05 Å.

(7) (a) C. Brosset, *Arkiv. Kemi. Mineral. Geol.*, **A20** (1945); (b) *ibid.*, **A22** (1946).

(8) J. A. Bertrand, F. A. Cotton, and W. A. Dollase, *Inorg. Chem.*, **2**, 1166 (1963).

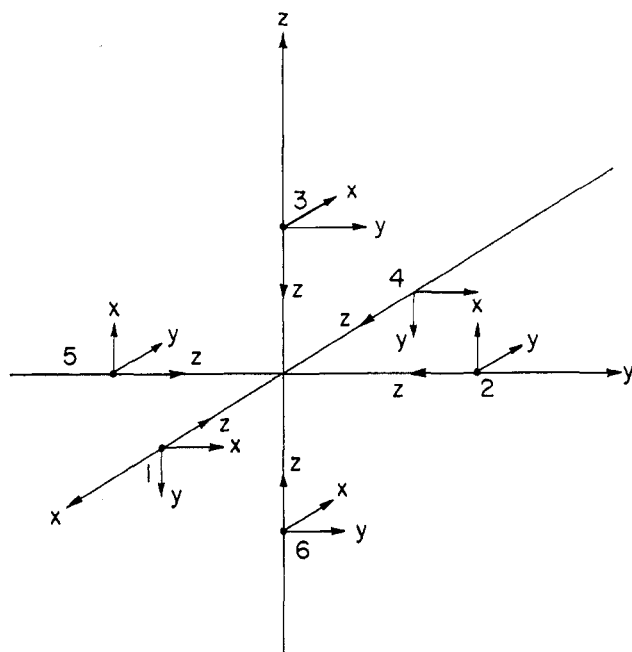


Fig. 1.—The general and local coordinate systems and the atom numbering for octahedral clusters.

accurate investigation of a molybdenum compound would be of interest to see if the reported difference in bond lengths is really so extreme. For the $[\text{NbX}_{12}]^{2+}$ and $[\text{Ta}_6\text{X}_{12}]^{2+}$ species, there are neither crystallographic nor chemical data bearing on the question of whether additional groups are bound.

Method of Calculation⁹

There are many ways in which one might elect to set up the secular equations for these molecules. The one we have chosen certainly involves some severe approximations, but we believe that it does not sacrifice any essential considerations while at the same time being quite tractable. We wish to stress, however, that we do not consider it to be more than a justifiable first approximation.

The initial conditions that we have deliberately set are the following. Each metal atom is assumed to use a $d_{x^2-y^2}$ or d_{xy} -orbital, an s-orbital, and the p_x - and p_y -orbitals to bind the four chlorine atoms which are arranged in a square array around it. This leaves p_z and the remaining d-orbitals for bonding to the other metal atoms of the cluster and for binding an additional ligand on the other side of the MX_4 plane. It has been further assumed that the d_{z^2} - p_z pair does not hybridize and that the centrifugally directed member is pure p_z , while the centripetally directed one is d_{z^2} . It will be seen later that this assumption, though it surely cannot be correct, has no qualitative effect on the results since the MO's arising from the d_{z^2} -orbitals are rather strongly bonding or antibonding and even fairly large fractional alterations in their energies would not alter the electron distribution patterns. Finally, we ignore any effect of interactions of the halogen $p\pi$ -orbitals with the various

(9) Additional details are presented in the thesis of T. E. Haas, M.I.T., 1963.

TABLE I
TRANSFORMATION PROPERTIES OF d-ORBITALS IN OCTAHEDRAL CLUSTERS

Orbital type	Irreducible representations
d_{z^2}	$A_{1g} + E_g + T_{1u}$
$d_{x^2-y^2}$	$A_{2g} + E_g + T_{2u}$
d_{xy}	$A_{2u} + E_u + T_{2g}$
(d_{xz}, d_{yz})	$T_{1g} + T_{2g} + T_{1u} + T_{2u}$

d-orbitals and take them all to have the same energy in isolated MX_4 units. We believe that the energy differences which must in reality exist should be small relative to the energy shifts produced by the interactions within the metal atom clusters.

We shall consider first the octahedral clusters and then the $[\text{Re}_3\text{Cl}_{12}]^{3-}$ system since it is convenient to use somewhat differently oriented local coordinate systems in the two types of compounds.

Octahedral Clusters.—It is first necessary to choose coordinate systems for these molecules. The choice made is illustrated in Fig. 1. It is not entirely arbitrary and was arrived at by placing atoms 1, 2, and 3 on the positive X, Y, and Z axes of the octahedron and atoms 4, 5, and 6 on the negative X, Y, and Z axes. For the local coordinate systems, at each metal atom, each z axis points toward the center of the octahedron. The local x and y axes are chosen so that each x axis points over an edge of the octahedron toward the atom of next higher number (modulo six). The y axes are then determined so that there are right-handed coordinate systems on atoms 1, 2, and 3 and left-handed ones on atoms 4, 5, and 6. With this choice of coordinates, in the $[\text{M}_6\text{X}_8]^{4+}$ system it is the four d-orbitals excepting d_{xy} which are available for metal-metal bonding, while in the $[\text{M}_6\text{X}_{12}]^{2+}$ systems it is the four d-orbitals other than $d_{x^2-y^2}$ which are to be used.

Utilizing standard group theoretical procedures, the representations spanned by sets of the five d-orbital types on the six atoms of the octahedra were determined and are summarized in Table I. Then, using d_{z^2} , d_{xz} , d_{yz} , and $d_{x^2-y^2}$ for $[\text{M}_6\text{X}_8]$ and d_{z^2} , d_{xz} , d_{yz} , and d_{xy} for $[\text{M}_6\text{X}_{12}]$, LCAO-MO wave functions with the appropriate transformation properties were constructed. It may be noted that for the $[\text{M}_6\text{X}_8]$ system, the T_{1u} , E_g , and T_{2u} representations occur twice, while in the $[\text{M}_6\text{X}_{12}]$ system, the T_{1u} and T_{2g} representations occur twice. Thus the secular equations are factored into mostly linear equations with only two or three quadratic ones.

The procedure for expressing the energies of these LCAO-MO's will now be illustrated. For the A_{1g} MO constructed from d_{z^2} -orbitals, we have

$$\psi = \sum_i \phi_i$$

Inserting this into the wave equation in the form

$$\int \psi \mathcal{H} \psi d\tau = E \int \psi \psi d\tau$$

and noting that all integrals $\int \phi_i \mathcal{H} \phi_i d\tau$ are equal (designated H_{11}), all integrals such as $\int \phi_1 \mathcal{H} \phi_2 d\tau$ between nearest neighbors are equal (H_{12}), and all integrals such

TABLE II

MOLECULAR ORBITAL ENERGIES ASSUMING $H_{ij} = 2H_{11}S_{ij}$

Atomic orbital type	Symmetry of MO	Energy
$d_{z^2}, d_{xy}, d_{x^2-y^2}$	A	$(1 + 8S_{12} + 2S_{14})/(1 + 4S_{12} + S_{14})$
	E	$(1 - 4S_{12} + 2S_{14})/(1 - 2S_{12} + S_{14})$
	T	$(1 - 2S_{14})/(1 - S_{14})$
d_{xz}, d_{yz}	T_{1g}	$(1 - 4S_{12} - 2S_{14})/(1 - 2S_{12} - S_{14})$
	T_{2g}	$(1 + 4S_{12} - 2S_{14})/(1 + 2S_{12} - S_{14})$
	T_{1u}	$(1 + 4S_{12} + 2S_{14})/(1 + 2S_{12} + S_{14})$
	T_{2u}	$(1 - 4S_{12} + 2S_{14})/(1 - 2S_{12} + S_{14})$

as $\int \phi_1 \mathcal{K} \phi_4 d\tau$ between second nearest neighbors are also equal (H_{14}), we obtain

$$6H_{11} + 24H_{12} + 6H_{14} = 6E(S_{11} + 4S_{12} + S_{14})$$

where S_{ij} is the overlap integral corresponding to H_{ij} and $S_{11} = 1$ because the ϕ_i are used in normalized form. If H_{11} is taken as the unit of energy and the often-used proportionality of energies to overlaps is taken in the form

$$H_{12} = 2H_{11}S_{12}$$

and

$$H_{14} = 2H_{11}S_{14}$$

we finally obtain

$$E_{A_{1g}} = \frac{1 + 8S_{12} + 2S_{14}}{1 + 4S_{12} + S_{14}}$$

Expressions were derived for all the LCAO-MO orbital energies by analogous procedures. The results are summarized in Table II.

It was next necessary to compute numerical values for the various overlap integrals, an undertaking which involved a considerable amount of tedious algebra. Expressions were derived for the desired S_{ij} in terms of the three basic kinds of tabulated overlap integrals, *viz.*, $S(d\sigma, d\sigma)$, $S(d\pi, d\pi)$, and $S(d\delta, d\delta)$; the details will not be given here.⁹ The results are collected in Table III. Since there were no self-consistent field wave functions available for the second and third transition series, it was necessary to use Slater type orbitals. As all metal atoms in a cluster are equivalent and there is only one characteristic internuclear distance, only the two parameters, α , the Slater orbital exponent, and R , the internuclear distance, are required. As usual, the product of these, $p = \alpha R$, is used as the variable in computing or looking up the overlap integrals. The $(5d\pi, 5d\pi)$ and $(5d\delta, 5d\delta)$ overlaps were found in tables,¹⁰ but the $(5d\sigma, 5d\sigma)$ integrals had to be computed. They are reported in Table IV. Since we shall be very much concerned about the sensitivity of the results to the choice of this parameter, the calculations have been carried out for a considerable range of p . Finally, as indicated above, the quantity H_{11} , which can be identified with the correct valence state ionization potential of the metal atom, is taken as the unit of energy, thus eliminating the need to know its actual magnitude, so long as only the qualitative features of the energy level scheme are of concern.

(10) H. H. Jaffé, *J. Chem. Phys.*, **21**, 258 (1953).

TABLE III

REQUIRED OVERLAP INTEGRALS FOR OCTAHEDRAL CLUSTERS AS SUMS OF TABULATED OVERLAP INTEGRALS^a

$$S_{12}(d_{z^2}, d_{z^2}) = \frac{1}{16}S(d\sigma, d\sigma) + \frac{3}{4}S(d\pi, d\pi) + \frac{3}{16}S(d\delta, d\delta)$$

$$S_{14}(d_{z^2}, d_{z^2}) = S(d\sigma, d\sigma)$$

$$-S_{12}(d_{x^2-y^2}, d_{x^2-y^2}) = \frac{3}{16}S(d\sigma, d\sigma) + \frac{3}{4}S(d\pi, d\pi) + \frac{1}{16}S(d\delta, d\delta)$$

$$S_{14}(d_{x^2-y^2}, d_{x^2-y^2}) = S(d\delta, d\delta)$$

$$-S_{12}(d_{xy}, d_{xy}) = \frac{1}{2}S(d\pi, d\pi) + \frac{1}{2}S(d\delta, d\delta)$$

$$S_{14}(d_{xy}, d_{xy}) = S(d\delta, d\delta)$$

$$-S_{12}(d_{xz}, d_{yz}) = S(d\sigma, d\sigma)$$

$$S_{14}(d_{xz}, d_{yz}) = S(d\pi, d\pi)$$

$$-S_{12}(d_{x^2-y^2}, d_{yz}) = \frac{1}{\sqrt{2}}S(d\sigma, d\sigma)$$

$$S_{12}(d_{z^2}, d_{yz}) = S_{12}(d_{xy}, d_{yz}) = 0$$

^a It is implicit that all tabulated overlaps are taken at appropriate values of the internuclear distance.

TABLE IV

5d σ -5d σ OVERLAP INTEGRALS FOR $l = 0$

p	S	p	S	p	S	p	S
0	1.000	5.25	0.192	10.25	0.330	15.50	0.047
.25	.991	5.50	.217	10.50	.312	16.00	.037
.50	.966	5.75	.243	10.75	.294	16.50	.029
.75	.926	6.00	.271	11.00	.276	17.00	.022
1.00	.871	6.25	.297	11.25	.257	18.00	.013
1.25	.806	6.50	.323	11.50	.239	19.00	.007
1.50	.732	6.75	.346	11.75	.221	20.00	.003
1.75	.654	7.00	.367	12.00	.204		
2.00	.573	7.25	.383	12.25	.187		
2.25	.494	7.50	.397	12.50	.172		
2.50	.419	7.75	.406	12.75	.157		
2.75	.350	8.00	.412	13.00	.142		
3.00	.290	8.25	.414	13.25	.129		
3.25	.239	8.50	.413	13.50	.117		
3.50	.199	8.75	.407	13.75	.105		
3.75	.171	9.00	.400	14.00	.095		
4.00	.153	9.25	.390	14.25	.085		
4.25	.145	9.50	.377	14.50	.076		
4.50	.146	9.75	.363	14.75	.068		
4.75	.156	10.00	.347	15.00	.060		
5.00	.171						

The $[\text{Re}_3\text{Cl}_{12}]^{3-}$ Cluster.—The general approach was the same as that used for the octahedral clusters. Relevant information is given in Tables V and VI. These results were obtained with the following choice of coordinate axes at the rhenium atoms. The z axis on each rhenium atom points to the center of the Re_3 triangle, the x axis lies in the plane of the triangle, and the y axes complete right-handed coordinate systems at all rhenium atoms.

TABLE V

TRANSFORMATION PROPERTIES OF THE d-ORBITALS OF THE RHENIUM ATOMS IN $[\text{Re}_3\text{Cl}_{12}]^{3-}$

Orbital type	Irreducible representations
d_{z^2}	$A_1' + E'$
d_{xy}	$A_1'' + E''$
d_{xz}	$A_2' + E'$
d_{yz}	$A_2'' + E''$

The results of the computations for the three types of system are presented graphically in Fig. 2, 3, and 4.

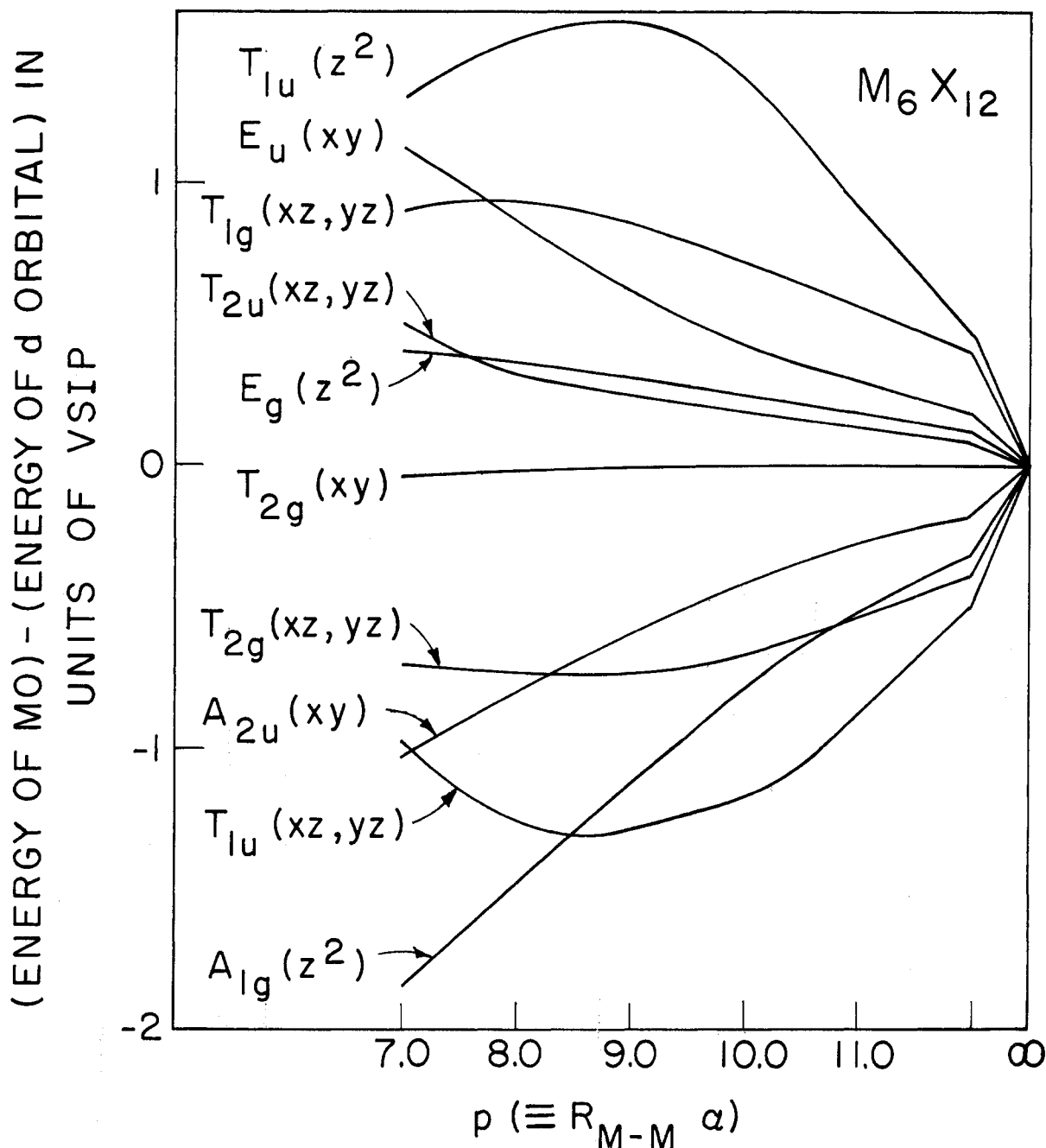
Fig. 2.—Molecular orbital energy level diagram for an M_6X_{12} system.

TABLE VI

REQUIRED OVERLAP INTEGRALS FOR TRIANGULAR CLUSTERS AS SUMS OF TABULATED OVERLAP INTEGRALS

$$S_{12}(d_{z^2}, d_{z^2}) = \frac{25}{64}S(d\sigma, d\sigma) + \frac{9}{16}S(d\pi, d\pi) + \frac{3}{64}S(d\delta, d\delta)$$

$$-S_{12}(d_{xy}, d_{xy}) = \frac{3}{4}S(d\delta, d\delta) + \frac{1}{4}S(d\pi, d\pi)$$

$$-S_{12}(d_{xz}, d_{xz}) = \frac{9}{16}S(d\sigma, d\sigma) + \frac{1}{4}S(d\pi, d\pi) + \frac{3}{16}S(d\delta, d\delta)$$

$$S_{12}(d_{yz}, d_{yz}) = \frac{3}{4}S(d\pi, d\pi) + \frac{1}{4}S(d\delta, d\delta)$$

$$S_{12}(d_{zz}, d_{yz}) = S_{12}(d_{xz}, d_{yz}) = 0$$

Discussion

From Fig. 2-4, it can be seen that the pattern of molecular orbitals in the clusters is *not* sensitive to the parameter p over the range used in the calculations insofar

as the numbers of bonding and antibonding MO's are concerned. Within these two categories, in each case, the ordering of the levels changes with p , but this will not be of significance in the following discussion. That the ranges chosen for p are realistic and likely to include all physically reasonable values is indicated by the following considerations. The metal-metal distances are in the range 2.45-2.90 Å., or about 5.0 ± 0.5 a.u. Thus, the range of p (7-12) corresponds to a range in α of about 1.5-2.2. Using Slater's rules, one calculates α values of 1.15-1.35 for Re^0 in the $5d^56s6p$ configuration, Mo^0 in the $4d^45s5p$, and Nb^0 in the $4d^55s5p$ configurations. Now these values obtained by Slater's rules are bound to be lower limits, for two reasons. First, the metal atoms must bear some fractional positive charge (on the order of +0.5) which tends to contract the d-

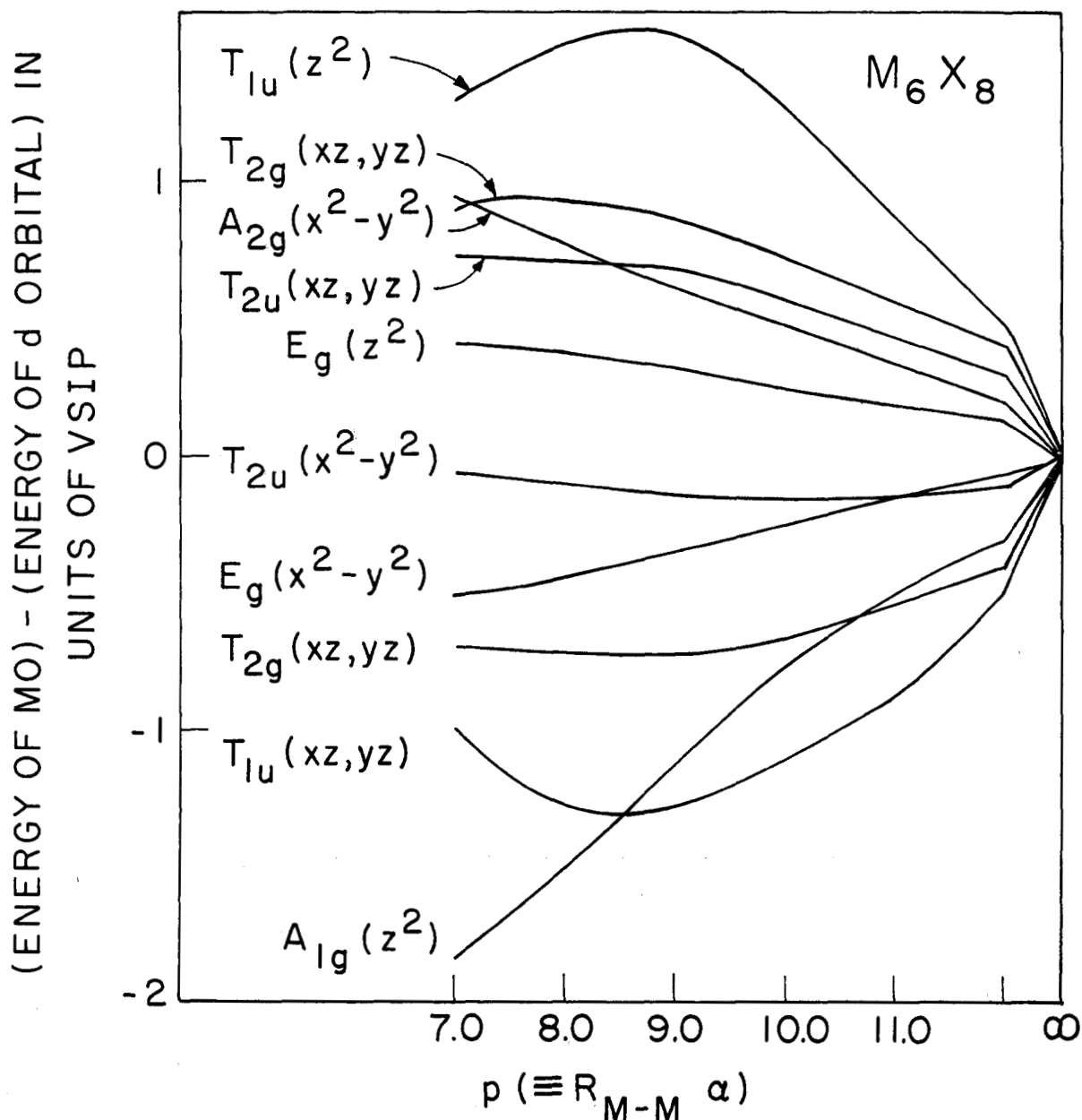


Fig. 3.—Molecular orbital energy level diagram for an M_6X_8 system.

wave functions, thus raising α by perhaps 0.1–0.2 unit, and, second, it is well known that Slater orbital exponents for d-orbitals run considerably smaller than those found by SCF methods.¹¹ Thus, a lower limit of 1.5 on the range of α is quite reasonable; of course the use of somewhat lower values would not alter the discussion which follows. The upper bound of about 2.2 was chosen to be, in our judgment, sufficiently beyond any physically reasonable upper limit.

Perhaps the most obvious criteria for the validity of the energy level schemes is that (1) they house the electrons so as to account for the experimentally observed number of unpaired electrons (none, in each of the three cases treated here) and (2) that they provide for filling of all bonding orbitals and nonfilling of all antibonding orbitals, with the fate of the nonbonding orbitals, if any, being less critical.

(11) R. E. Watson, *Phys. Rev.*, **119**, 1984 (1960).

The results we have obtained satisfy these criteria in all cases. As we have noted, in the $[M_6X_{12}]^{2+}$ systems there are 16 electrons to occupy the MO's of the cluster. These just fill the bonding orbitals A_{1g} , A_{2u} , T_{1u} , and T_{2g} . In the $[M_6X_8]^{4+}$ system, there are 24 electrons to occupy MO's of the cluster and these are just sufficient to fill all of the strongly bonding orbitals, A_{1g} , T_{1u} , T_{2g} , and E_g as well as the T_{2u} orbital which is shown in Fig. 3 as only weakly bonding, but see the next paragraph for an important qualification in this connection. In $[Re_3Cl_{12}]^{3-}$, there are twelve electrons and just six bonding MO's.

It should further be noted that the empty nonbonding T_{2g} -orbital shown in the diagram for the M_6X_{12} system most likely has appreciable antibonding character as a result of interaction with the bonding T_{2g} orbital. That this interaction is not strongly exhibited in the results may be regarded as a fiction of the overlap approxima-

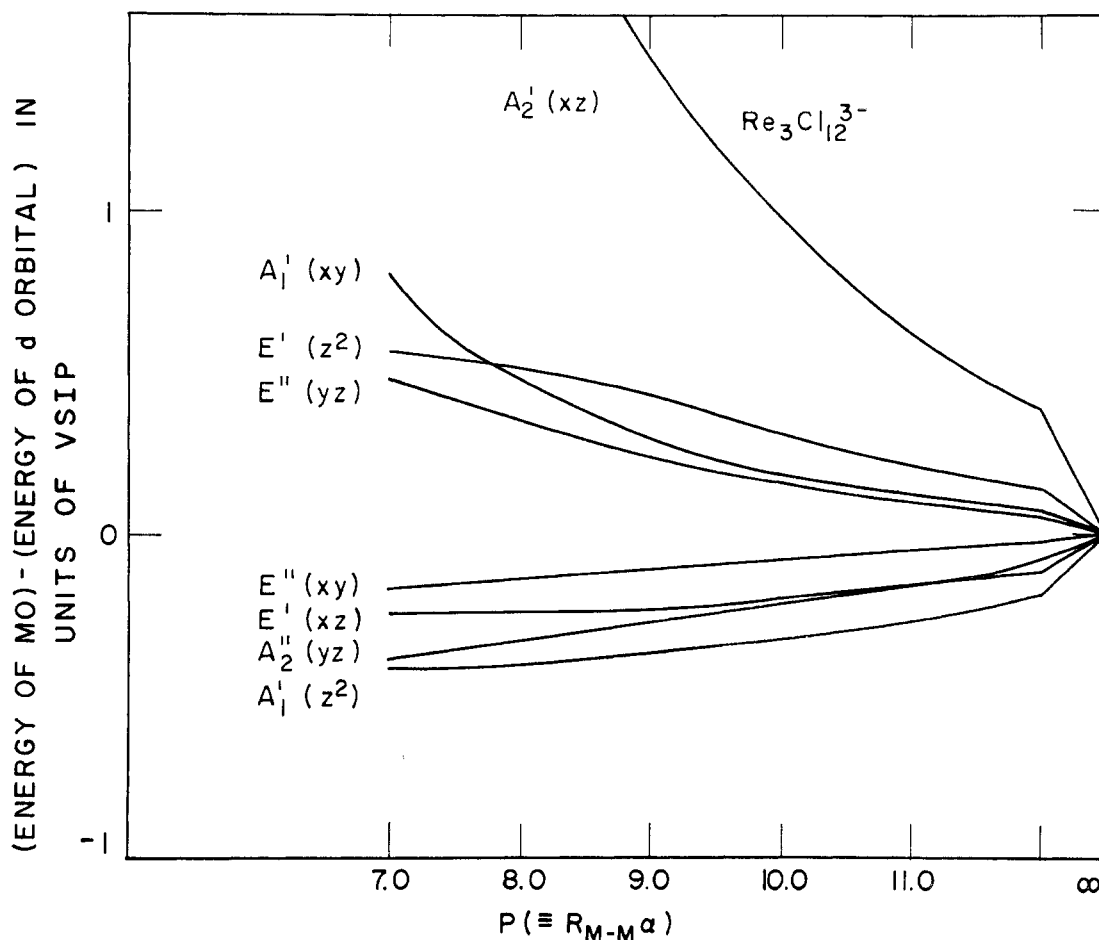


Fig. 4.—Molecular orbital energy level diagram for an M_3X_{12} system.

tion used in the calculations, since the overlap integral between the d_{xy} -orbitals from which the upper T_{2g} MO is formed and the d_{xz} - and d_{yz} -orbitals from which the lower T_{2g} state is formed is zero. Similarly, in the M_6X_8 case, configuration interaction between the T_{2u} MO's should depress the lower, filled one, making it more strongly bonding.

The marked qualitative difference in the arrangement of molecular orbitals in the two octahedral clusters despite the small difference in the sets of atomic orbitals from which they are constructed is interesting. The sole difference in the basis sets is a 45° rotation of one d-orbital on each metal atom about the local z axis, yet the result is a difference of four bonding orbitals. No graphic or pictorial explanation of this is evident to us.

The results presented here for known systems invite discussion as to the possibility of predicting the existence of other, as yet uncharacterized metal atom cluster compounds. While we shall not undertake an exhaustive treatment of this problem here, several fairly obvious observations can be made. Clearly, congeneric systems are to be looked for. For example, the trihalides of technetium and the dihalides of tungsten may form cluster compounds. The former would lead into some quite new chemistry in any event, since Tc^{III} chemistry seems hardly to have been explored. Regarding tungsten, we previously⁸ speculated that the reported compound $K_5W_3Cl_{14}$ ¹² might in fact be K_6W_3-

Cl_{12} with a $[W_3Cl_{12}]^{6-}$ ion isostructural with $[Re_3Cl_{12}]^{3-}$. In view of the charge considerations discussed below, we are less inclined to favor the existence of such a complex anion¹³ and believe it more likely that the W^{II} halides will be structurally analogous to those of molybdenum.

As for cluster compounds of the known types with metals not congeneric with those already discussed, the possibilities are somewhat limited if high charges are to be avoided. Thus, a group IV metal, say Zr or Hf, might form an $[M_6Cl_{12}]^{4-}$ ion, but it seems less likely that a group VI metal would form an $[M_6Cl_{12}]^{3+}$ ion. Similarly, the M_6X_8 cluster might exist with a group V metal, *viz.*, $[M_6X_8]^{2-}$, but is less likely with a group VII metal, *viz.*, $[M_6X_8]^{10+}$. If, however, it is also important that the M_6X_{12} , M_6X_8 , or M_3X_9 cluster be positively charged or neutral, the existence of a negative charge on the cluster may also be disallowed. Finally, however, it may also be possible that each centrifugally directed orbital can be occupied by an unshared electron pair, thus making possible a species such as $[M_6X_8]^{4+}$ where M is Ru or Os in a formal oxidation state of II.

A possible example of the influence of the over-all charge on the structure of the metal atom cluster may be found on comparing the $[Mo_6Cl_8]^{4+}$ and $[Re_3Cl_{12}]^{3-}$

(13) It also appears that the material " $K_5W_3Cl_{14}$ " may not contain any new polynuclear complex. Dr. E. König of Mellon Institute has informed us that he has evidence indicating it to be a mixture of $K_5W_3Cl_9$ and $K_3W_3Cl_5(OH)$.

ions. Mo^{II} and Re^{III} , which are the species formally present in the two cases, are isoelectronic (d^4). However, if each were to adopt the other's structure, we should have $[\text{Mo}_3\text{Cl}_{12}]^{6-}$ and $[\text{Re}_3\text{Cl}_9]^{10+}$. The charges in both cases are quite high, and, in the former case, there is the added consideration that even the $[\text{Mo}_3\text{Cl}_9]^{3-}$ core would have a substantial negative charge, so that it would be unlikely to combine with 3Cl^- to give $[\text{Mo}_3\text{Cl}_{12}]^{6-}$.

In summary, the combined requirements of filling only the bonding molecular orbitals and satisfying electrostatic requirements may place very severe restrictions on how many metal atom clusters are capable of existence. Nonetheless, chemical studies of the lower oxidation states of the heavier transition metals should be carried out with at least some alertness to the possibility of encountering further metal atom cluster compounds.

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Molecular and Electronic Structures of Some Thiourea Complexes of Cobalt(II)^{1a}

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Five thiourea (TU) complexes of cobalt(II) have been prepared and studied spectroscopically and magnetically. The results of spectroscopic and magnetic studies show that $\text{Co}(\text{TU})_2\text{Cl}_2$, $\text{Co}(\text{TU})_2\text{Br}_2$, $[\text{Co}(\text{TU})_4](\text{ClO}_4)_2$, and $[\text{Co}(\text{TU})_3\text{SO}_4]$ contain tetrahedrally coordinated sulfur. It is also shown that thiourea occupies a position comparable to various oxygen ligands near the low end of the spectrochemical series and that, like some other sulfur ligands, it causes an exceptionally large nephelauxetic effect ($\beta_{35} \leq 0.6$). $\text{Co}(\text{TU})_4(\text{NO}_3)_2$ is shown to be an octahedral complex, though superficial interpretation of the reflectance spectrum might have suggested otherwise. Interpretation of the spectrum using an octahedral model necessitates the assumption of a very large nephelauxetic effect ($0.51 < \beta_{35} < 0.62$). This interpretation is substantiated by results for the similar complex $[\text{Ni}(\text{thiourea})_6](\text{NO}_3)_2$ for which $\beta_{35} \approx 0.65$.

Introduction

Thiourea (TU) complexes of cobalt(II) were apparently first studied by Rosenheim and Meyer,² who reported $\text{Co}_2(\text{TU})_7\text{Cl}_4$, $\text{Co}(\text{TU})_4(\text{NO}_3)_2$, and $\text{Co}_2(\text{TU})_3(\text{SO}_4)_2$. In a study of the phases of the CoCl_2 -thiourea-water system at 35° , $\text{Co}_2(\text{TU})_7\text{Cl}_4$ was reported again along with $\text{Co}(\text{TU})_2\text{Cl}_2$.³ Both compounds were reported to be blue. $\text{Co}_2(\text{TU})_7\text{Cl}_4$ was stated to have a molar magnetic susceptibility of $17,420 \times 10^{-6}$ c.g.s. unit at 35° with a magnetic moment of 3.77 B.M. These two numbers are inconsistent, however; assuming the susceptibility to be correct, $\mu_{\text{eff}} = 4.66$ B.M. per cobalt atom. For $\text{Co}(\text{TU})_2\text{Cl}_2$ the molar susceptibility was reported to be 6719×10^{-6} c.g.s. unit at 35° , giving a moment of 4.05 B.M. A moment of this magnitude is inconsistent with any of the three plausible assumptions for the coordination geometry, *viz.*, octahedral,⁴ tetrahedral,⁵ or planar.⁶ The compounds $\text{Co}(\text{TU})_2(\text{NCS})_2$ and $\text{Co}(\text{TU})_4\text{Cl}_2$ have been reported and their structures proved (by comparison with the known structures of isomorphous nickel complexes) by

Nardelli, *et al.*⁷⁻¹⁰ It has also been shown⁸ that $\text{Co}_2(\text{TU})_7\text{Cl}_4$ is actually $\text{Co}(\text{TU})_4\text{Cl}_2$. When the appropriate correction is applied to the moment of 4.66 B.M. given above for $\text{Co}_2(\text{TU})_7\text{Cl}_4$ it becomes 4.87 B.M., which is in good agreement with the value of μ_{eff} at room temperature obtained in this laboratory¹¹ previously, namely, 4.90 B.M.

From these fragmentary results, it appeared that a more detailed investigation of thiourea complexes, along lines previously followed for other cobalt(II) complexes,^{5,12} would prove fruitful.

Experimental

Preparation of Compounds. $\text{Co}(\text{thiourea})_4(\text{NO}_3)_2$.— $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (2.91 g., 0.01 mole) was dissolved in 25 ml. of hot butanol, 3.04 g. (0.04 mole) of thiourea was added, and the mixture heated to boiling, until all solid had dissolved, the solution changing from red to blue. On cooling, a blue solid separated. This was suction filtered, washed with ether, dried under vacuum, and then recrystallized from ethyl acetate. This produced large green-blue crystals which were ground and dried under vacuum at 100° ; yield 4.4 g. The compound is soluble in hot ethyl acetate, acetone, and hot acetonitrile, giving purple solutions. It is decomposed by nitromethane and is insoluble in tetrahydrofuran, carbon disulfide, and methylene chloride.

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