enabled such structures to be determined with fair certainty, much less is known about the reasons for the adoption of a particular structure.[2] We believe that this work on complexes of nickel with substituted thioureas has perhaps raised more questions than provided answers in this respect.

Why, for example, do the octahedral compounds $[NiS_4X_2]$ change to the less common tetrahedral structure in solution? A similar equilibrium has recently been shown to occur with several cobalt complexes[29]; cobalt is, of course, well known to frequently favor a tetrahedral structure. These authors indicate that they also have evidence for a simple tetrahedral–octahedral configuration equilibrium for nickel in solution, and are investigating the thermodynamics of the equilibrium.

It would be useful if we could sort out the steric factor from the polarizability of the ligands in determining stereochemistry, but this is very difficult. Thus, the fact that both $[Ni(naptu)_2Br_2]$ and $[Ni(naptu)_2I_2]$ are tetrahedral rather than octahedral like the chloride complex formed by naphthylthiourea could be ascribed to steric factors (the larger size of bromide and iodide *vs.* chloride), or perhaps the larger polarizability, and presumably more covalency, helps to favor the tetrahedral structure. Other factors, such as the relative stability of the solid phases, may of course also be important.

On the other hand, the donor atom in ethylenethiourea is really about as polarizable as iodide, or at least the two ligands neighbor each other in the nephelauxetic series,[1] yet the regular octahedral $[Ni(etu)_6](ClO_4)_2$ is formed. This suggests that highly polarizable ligands alone cannot force nickel to attain a tetrahedral structure, and that steric factors may be more important.

That the situation is not straightforward is readily realized when we try to account for the fact that nickel may also attain a planar geometry. Thus, while both $[Ni(naptu)_2Br_2]$ and $[Ni(quinoline)_2Br_2]$ are tetrahedral, we find $[Ni(naptu)_2I_2]$ is tetrahedral while $[Ni(quinoline)_2I_2]$ is planar.[2] That the factors which determine square-planar *vs.* tetrahedral stereochemistry are finely balanced is evidenced by several recent expositions of solution equilibria between the two structures.[30]

We believe that ethylenethiourea is the first ligand which has been shown to be capable of forming either planar, $[Ni(etu)_4](ClO_4)_2$, or octahedral, $[Ni(etu)_6](ClO_4)_2$, structures. We see no ready explanation for the formation of both of these.

That $[Ni(etu)_4I_2]$ is tetragonal (diamagnetic) while $[Ni(etu)_4X_2]$ (X = Cl, Br) are octahedral can probably be explained by a consideration of the position of the ligands in the spectrochemical series. Since ethylenethiourea is closest to chloride in this series,[1] the average ligand field is nearest to octahedral in $[Ni(etu)_4Cl_2]$, while the average ligand field approximation is probably poor in the case of the iodide.

Lastly, why is $[Ni(etu)_4Cl_2]$ (yellow) a normal octahedral molecule while $[Ni(detu)_4Cl_2]$ exhibits a weak tetragonal field?[5] Electronically, the constriction of tying back the ethyl groups (in ethylenethiourea) is only a second-order effect at the donor sulfur atom, and we think that this does not cause the change in electronic structure (crystalline field) at the nickel. Rather, we think the important factor may be that of steric crowding among the diethylthiourea molecules. Complete crystal structure analyses of these two compounds should prove to be very interesting.

Acknowledgment.—We thank L. M. Swink for help with the X-ray work. This work was supported by a grant from the National Science Foundation.

(29) H. C. A. King, E. Körös, and S. M. Nelson, *J. Chem. Soc.*, 5449 (1963).

(30) D. R. Eaton, W. D. Phillips, and D. J. Caldwell, *J. Am. Chem. Soc.*, **85**, 397 (1963); R. H. Holm and K. Swaminathan, *Inorg. Chem.*, **2**, 181 (1963).

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The Crystal, Molecular, and Electronic Structures of a Binuclear Oxomolybdenum(V) Xanthate Complex[1]

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The crystal and molecular structures of $[(C_2H_5OCS_2)_2MoO]_2O$, a binuclear, oxo-bridged complex of molybdenum(V), have been determined by single crystal X-ray diffraction methods, including least-squares refinement of atomic positional parameters and isotropic thermal vibration parameters. The space group is $P2_1$, $Z = 2$, and the unit cell dimensions are $a = 10.72 \pm 0.03$, $b = 13.57 \pm 0.03$, $c = 10.86 \pm 0.03$ Å., $\beta = 123.5 \pm 0.5°$. The electronic structure of this molecule as a function of the internal angle of twist has been investigated by the Hückel LCAO–MO method and it is shown that the diamagnetism can be accounted for. It is also shown that this treatment leads to a possible explanation for the reported existence of both diamagnetic and paramagnetic dimeric Mo(V) species in HCl solutions of Mo(V).

Introduction

In 1939, Malatesta[3] reported a molybdenum complex of ethyl xanthate with the formula $Mo_2O_3(S_2COC_2H_5)_4$. The structure of this compound appeared to us to be worthy of investigation for many reasons, including (1) the probable presence of both Mo—O and Mo=O bonds; (2) the probable presence of an Mo—O—Mo group, the linearity of which is of interest; (3) the need of knowing the molecular structure and orientation in order to interpret the electronic structure of the compound, which is diamagnetic; (4) the importance of structural information on Mo(V) and Mo(VI) complexes in understanding the behavior of molybdenum

(1) Supported by the National Institutes of Health.

(2) Fellow of the Alfred P. Sloan Foundation.

(3) L. Malatesta, *Gazz. chim. ital.*, **69**, 408 (1939).

as it participates in various enzymatic reactions[4]; and (5) the light which detailed knowledge of this molecule might throw on the nature of other molybdenyl compounds, as well as on compounds with metal-to-oxygen multiple bonding in general.

Experimental

Single crystals suitable for X-ray analysis were obtained by slow evaporation of solutions of the complex in tetrachloroethylene. From zero and upper level precession photographs, they were found to be monoclinic with the following unit cell dimensions: $a = 10.72 \pm 0.03$, $b = 13.57 \pm 0.03$, $c = 10.86 \pm 0.03$ Å., and $\beta = 123.5°$. The approximate density (determined by flotation in aqueous $NaHgI_4$ solution containing *ca.* 1.1 g. cm.$^{-3}$) was 1.8 g. cm.$^{-3}$. Taking the molecular weight as 724, $Z = 2$ and the calculated density is 1.827 g. cm.$^{-3}$.

The systematic absences, $0k0$ for $k = 2n + 1$, indicated space group $P2_1$ (No. 4) or space group $P2_1/m$ (No. 11). While comparison of the statistical distribution of intensities from the 100 and 001 zones with the theoretical distributions discussed by Hargreaves[5] for structures containing heavy atoms suggested that the centrosymmetric space group might be the correct one, a positive piezoelectric test indicated that the structure was almost certainly acentric.

Intensities were recorded photographically using the precession method and Mo $K\alpha$ radiation. Using a small crystal, of maximum dimension *ca.* 0.3 mm., mounted about the crystal y axis, the reciprocal lattice levels $hk0$ through $hk3$, $0kl$ through $3kl$, and $hk\bar{h}$ through $hk(\bar{h} + 3)$ were recorded. In order to cover the complete range of intensity, several photographs of each level were taken, varying in exposure from 1 to 48 hr. All intensities were estimated visually by comparison with a set of timed exposures of the 040 reflection, and measurements were confined to those reflections with $0 < \sin \theta/\lambda \leqslant 0.5$ (there being very few reflections of measurable intensity outside this range). No corrections were made for absorption, the linear absorption coefficient, μ, being 16 cm.$^{-1}$. Of approximately 1340 independent reflections in this region of reciprocal space, 1260 were accessible on the reciprocal levels mentioned above.

Lorentz-polarization corrections were than applied, using a program written for the IBM 709/7090 by A. B. B. In addition to calculating the Lorentz-polarization corrections, this program also placed all films onto the same relative scale, by comparison of the intensities of reflections common to two or more films, and then converted all the relative $|F|^2$ values to an approximately absolute scale, using Wilson's method.[6]

Structure Determination

A three-dimensional Patterson synthesis was first computed using the measured $|F|^2$ values. This calculation and all subsequent electron density summations were carried out using the Fourier program, ERFR-2.[7] From the Patterson synthesis, it was immediately evident that the distribution of the heaviest vector peaks corresponded to the space group $P2_1$; for the absence of a peak, sufficiently large to be an Mo–Mo interaction, along the line $0,y,0$, ruled out $P2_1/m$. Taking the molybdenum atom coordinates as x_1, 0, z_1, and x_2, y_2, z_2, the heaviest vectors (apart from the origin) were those expected for single weight Mo–Mo interactions, namely, the Harker peaks $2x_{1 \text{ or } 2}$, $^1/_2$, $2z_{1 \text{ or } 2}$ and the peaks $x_2 - x_1$, y_2, $z_2 - z_1$ and $x_2 + x$, $^1/_2 - y_2$, $z_2 + z_1$. In addition to the Harker section $P(x, {}^1/_2, z)$ the section $P(x, 0, z)$ also showed very high vector density and suggested that the xanthate groups were parallel or nearly so, to the xz plane, and approximately normal to the molybdenum–molybdenum axis. The more prominent peaks in these two sections were taken as possible candidates for molybdenum–sulfur vectors (these being double weight when $y = 0$ or $^1/_2$). Assuming a molybdenum–sulfur bond of *ca.* 2.5 Å., coordinates were derived for four sulfur atoms around one of the molybdenum atoms (so that the two xanthate groups were *trans*) and for three of the sulfur atoms around the second molybdenum atom. These nine atoms were then used to derive phases to enable a three-dimensional electron density distribution to be calculated. This first Fourier indicated that the chosen positions for six of the seven sulfur atoms were almost certainly correct, but that the maximum of electron density for the seventh lay much too close to the molybdenum to be considered as a sulfur atom. In addition, two heavy peaks appeared, one for each molybdenum atom, which indicated fairly clearly that in both halves of the molecule the two xanthate groups were *cis* to each other. The above mentioned peak was thus taken as being an oxygen atom. At this stage, there was no clear evidence of the oxygen atom linking the two halves of the molecule, but in any event, this was expected to be disturbed by series termination errors from the two molybdenum atoms. The eleven atoms derived above were included in a structure factor calculation for which the residual, R, stood at 0.45.

A second three-dimensional electron density summation established the eight sulfur atoms at distances of *ca.* 2.6 Å. from the molybdenum atoms and revealed the remaining atoms of one xanthate group and the "ring" carbon atoms and oxygen atoms of two other groups, the peak electron densities of these atoms being lower than those of the former group. Although it was anticipated that due to the predominance of the molybdenum and sulfur atoms, sufficient phases would be correct at this stage to give a clear indication of the positions of all the light atoms in the molecule, apart from those mentioned above, there was no definite evidence of the remainder. A structure factor calculation based on a total of nineteen atoms showed little improvement and a difference synthesis, based on the output, revealed only the "bridging" oxygen atom between the two molybdenum atoms and the second nonbridging oxygen atom, whose position had hitherto been in doubt.

It was thus decided to refine the positional and thermal parameters of the molybdenum and sulfur atoms. One cycle of full-matrix least-squares refinement (39 variables) was accordingly carried out[8] and this produced radical changes in the positional parameters of the sulfur atoms and in the thermal parameters of all atoms. A structure factor calculation based on the new parameters for these ten atoms gave a residual of 0.23. A three-dimensional difference synthesis clearly revealed all the light atoms except for the outermost carbon atoms of two of the xanthate groups. However, these became clear after one more cycle of Fourier refinement and the residual for all 29 atoms stood at 0.165. A cycle of full-matrix least-squares refinement of all positional and thermal parameters (one isotropic temperature factor per atom) produced very large shifts in these parameters for the

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

(5) A. Hargreaves, *Acta Cryst.*, **8**, 12 (1955).

(6) A. J. C. Wilson, *Nature*, **150**, 152 (1942).

(7) W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two and Three Dimensional Fourier Summation Program for the IBM 709/7090-ERFR-2," 1962.

(8) C. T. Prewitt, "A Full-Matrix Least Squares Refinement Program for the IBM 709/7090 Computer," 1962.

Table I

Final Atom Parameters and Their Standard Deviations

Atom	x	y	z	B, Å.^{2}	$\sigma_x \times 10^4$	$\sigma_y \times 10^4$	$\sigma_z \times 10^4$	σB
Mo(1)	0.23642	0.0	0.08156	4.34	3.5	0	3.5	0.08
Mo(2)	.28520	.26739	.17356	4.26	3.4	2.8	3.4	.08
O(1)	.2584	.1327	.1285	4.69	31	24	35	.55
O(2)	.0972	− .0062	− .0929	5.74	26	23	26	.61
O(3)	.1635	.3179	.0121	4.82	27	20	27	.57
S(1)	.1684	− .0362	.2591	5.40	12	8.3	12	.26
S(2)	.2402	− .1844	.1181	4.87	12	8.2	12	.25
C(1)	.1836	− .1543	.2336	4.18	44	29	44	.91
O(4)	.1557	− .2296	.3024	5.05	25	19	26	.56
C(5)	.1676	− .3311	.2723	6.63	53	34	53	1.22
C(6)	.1512	− .3865	.3774	7.97	55	44	63	1.38
S(3)	.41985	− .0039	.0067	4.76	10.5	9.3	10.8	0.22
S(4)	.5212	− .0182	.3134	4.57	10.8	8.6	10.7	0.23
C(2)	.5555	− .0159	.1910	4.53	46	38	45	1.07
O(5)	.6998	− .0091	.2231	5.40	32	27	32	0.74
C(7)	.7310	.0003	.1072	10.81	63	52	68	1.63
C(8)	.7802	.1028	.0983	13.10	79	59	86	1.97
S(5)	.5343	.2586	.2117	4.35	11	9	11.5	0.23
S(6)	.43325	.4207	.3104	4.68	11.5	8.5	11.5	.24
C(3)	.5692	.3663	.2953	4.21	43	28	42	.88
O(6)	.7064	.4099	.3612	4.58	27	20	26	.57
C(9)	.8311	.3670	.3605	7.67	60	39	56	1.37
C(10)	.9655	.4337	.4597	5.52	48	33	48	1.10
S(7)	.11805	.2844	.2668	5.28	12	10	12	0.26
S(8)	.4156	.2011	.4547	4.57	11	8	11	0.23
C(4)	.2631	.2332	.4284	6.52	46	33	47	1.06
O(7)	.2389	.2268	.5427	4.96	28	19	29	0.66
C(11)	.3573	.2019	.6946	10.50	70	47	72	1.70
C(12)	.2977	.2320	.7859	12.90	68	49	70	1.88

light atoms and dropped the residual to 0.115. Weighting of the data seemed appropriate at this point and this was carried out using the function $w = 1/(10/F_o + F_o/40)$. This function downweights reflections with small F_{obsd} and very large F_{obsd} and gives maximum weight to planes of intermediate magnitude, which are believed to be the more reliable.

A further cycle of least-squares refinement with weighting lowered the residual to 0.098 and predicted further appreciable shifts in the positional parameters of some of the light atoms of the xanthate groups. The predicted changes in the majority of the other parameters were less than their standard deviations. A structure factor calculation, based on the new parameters, showed little change in R and R' and a three-dimensional difference Fourier was calculated to check for the absence of any major anomalies. As expected, the difference map showed anomalies characteristic of anisotropic thermal motion in the light atoms, but, more important, indicated that slight changes in some of their positional parameters (especially the outermost carbon atoms) were still necessary. These changes were accordingly made and a final cycle of refinement indicated that convergence of all parameters to their final values had now been reached. The final value of the residual, R, is 0.088 and of the weighted, R', is 0.086. The atomic scattering factors used in this analysis were for molybdenum that tabulated by Thomas and Umeda,[9] corrected for the real part, $\Delta f'$, of anomalous dispersion,[10] for sulfur that tabulated by Berghuis, *et al.*,[11] and for carbon and oxygen those tabulated by Hoerni and Ibers.[12]

All reflections were used in the least-squares refinement, those of zero observed intensity on the films being included as $^2/_3$ of the minimum value observed in the surrounding region of reciprocal space. The final position and thermal parameters obtained, together with their standard deviations, are listed in Table I, B_i being the isotropic temperature factors in the expression $\exp(-B_i \sin^2 \theta/\lambda^2)$. The standard deviations are obtained from the usual least-squares formula

$$\sigma^2(j) = a_{jj}(\Sigma w\Delta^2)/(m - n)$$

where a_{jj} is the appropriate element of the matrix inverse to the normal equation matrix. The final values of the calculated structure factors and the absolute values of the observed structure factors have been deposited with the American Documentation Institute.[13]

Discussion

The general structure of the molecule, Fig. 1 and 2, can be described crudely as consisting of two distorted octahedra[14] sharing an oxygen atom so as to form a

(9) L. F. Thomas and K. Umeda, *J. Chem. Phys.*, **26**, 239 (1957).

(10) C. H. Dauben and D. H. Templeton, *Acta Cryst.*, **8**, 841 (1955).

(11) J. Berghuis, IJ. M. Haanappel, M. Potters, B. O. Loopstra, C. H. MacGillavry, and A. L. Veenendaal, *ibid.*, **8**, 478 (1955).

(12) J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

(13) A table of observed and calculated structure factors has been deposited as Document 7933 with the American Documentation Institute, Auxiliary Publication Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting in advance $1.25 for photoprints or $1.25 for 35-mm. microfilm, payable to Chief, Photoduplication Service, Library of Congress.

(14) In view of the results recently obtained for $Co(Me_3PO)_2(NO_3)_2$ [F. A. Cotton and R. H. Soderberg, *J. Am. Chem. Soc.*, **85**, 2402 (1963)], $(AsPh_4)[Co(NO_3)_4]$ (J. G. Bergman and F. A. Cotton, to be published), and $Ce_2Mg_3(NO_3)_{12}\cdot24H_2O$ [A. Zalkin, J. D. Forrester, and D. H. Templeton, *J. Chem. Phys.*, **39**, 2881 (1963)], the plausibility of considering each xanthate group to be occupying one position of a tetrahedron with the oxygen atoms at the other two was also examined. Taking the bonds to the xanthates to be directed toward their carbon atoms, the six bond angles turn out to be: O(1)Mo(1)O(2), 105°; O(1)Mo(1)C(1), 126°; O(1)Mo(1)C(2), 91°; C(1)Mo(1)C(2), 110°; O(2)Mo(1)C(1), 106°; O(2)Mo(1)C(2), 124°. Thus the actual configuration is far more distorted from this "tetrahedral" ideal structure than from the idealized octahedral one we have chosen.

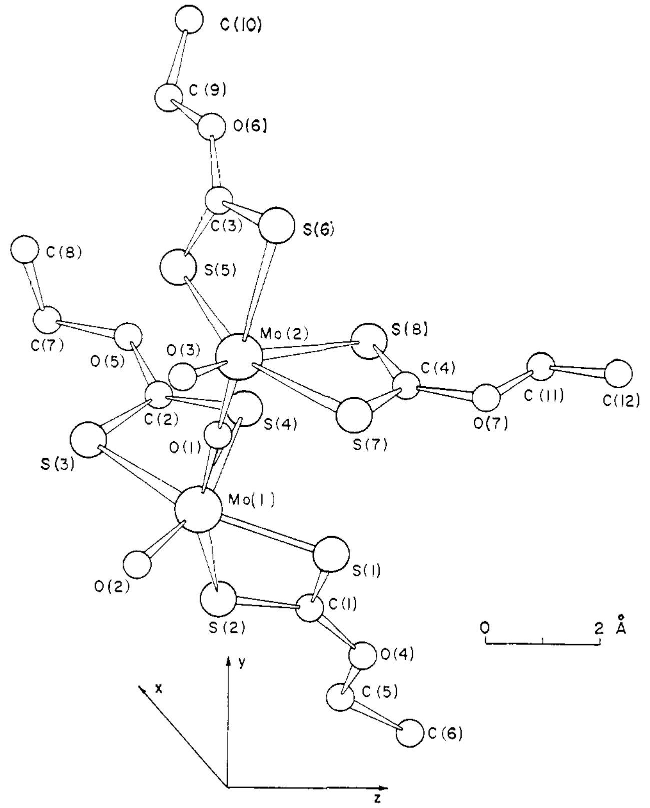

Fig. 1.—A perspective view of the $Mo_2O_3(S_2COC_2H_5)_4$ molecule. Numbers identify the atoms in Tables I, II, and III.

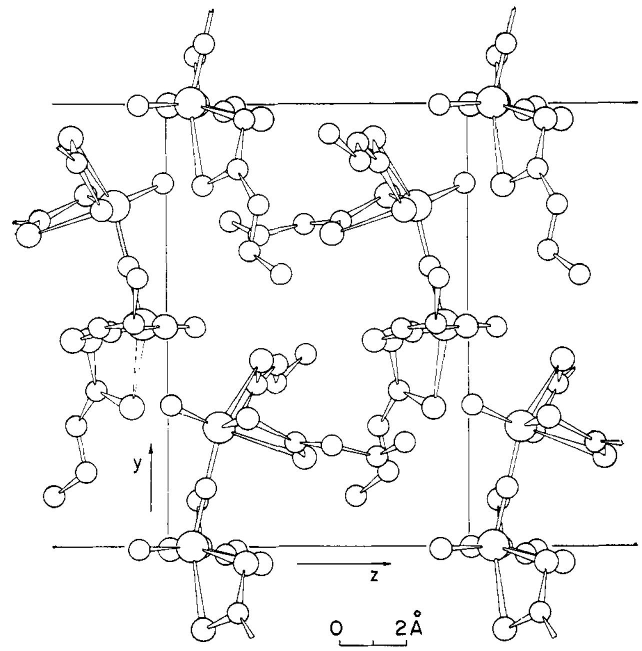

Fig. 2.—The contents of the unit cell projected perpendicular to the x axis.

linear Mo–O–Mo group. There is then a second oxygen atom on each molybdenum atom *cis* to the bridging one and the remaining four atoms bound to each molybdenum atom are xanthate sulfur atoms. For convenience in the following discussion we shall call the bridging oxygen atom O_b and the other, terminal ones, O_t.

The molecule is not crystallographically required to possess any symmetry elements whatever. In fact, it comes very close to having a twofold axis through O_b and bisecting a line connecting the O_t atoms. Thus, although the four xanthate ions are all crystallographically independent, as are the two Mo–O_t and two Mo–O_b bonds, they can be grouped in pairs, the members of each pair being related by the pseudo-twofold axis.

Coordination of the Molybdenum.—Table II gives the values of all the bond lengths and interbond angles for the bonds to the molybdenum atoms. It is evident that corresponding dimensions in the two halves of the molecule are all identical within the limits of significance.

The mean Mo–O_t bond length is 1.65 ± 0.02. The mean of the Mo–O_b distances is 1.86 ± 0.02. The former is by far the shortest *reliable* M–O distance found thus far when M is from the second or third transition series.[15] For comparison, the Mo–O distances in $MoO_3\cdot$dien[16] are 1.737 ± 0.005, while that in the MoO_4^{2-} ion in $PbMoO_4$ is reported[17] to be 1.77 with an unspecified but presumably very small ESD. The few other reported Mo–O distances are subject to much greater and inadequately known uncertainties. The significance of these four rather accurate Mo–O distances, in relation to bond orders and force constants, will be discussed in a later paper.

TABLE II

BOND LENGTHS AND BOND ANGLES AROUND THE MOLYBDENUM ATOMS[a]

Bond lengths, Å.			
Mo(1)–S(1)	2.458 ± 0.013	Mo(2)–S(5)	2.469 ± 0.013
Mo(1)–S(2)	2.530 ± .013	Mo(2)–S(6)	2.540 ± .013
Mo(1)–S(3)	2.509 ± .012	Mo(2)–S(7)	2.508 ± .014
Mo(1)–S(4)	2.690 ± .012	Mo(2)–S(8)	2.715 ± .012
Mo(1)–O(1)	1.851 ± .034	Mo(2)–O(1)	1.872 ± .034
Mo(1)–O(2)	1.644 ± .029	Mo(2)–O(3)	1.649 ± .028
Interbond angles, deg.			
O(1)–Mo(1)–S(1)	91.48 ± 1.11	O(1)–Mo(2)–S(5)	89.56 ± 1.10
O(1)–Mo(1)–S(3)	96.11 ± 1.10	O(1)–Mo(2)–S(7)	98.89 ± 1.10
O(1)–Mo(1)–S(4)	85.71 ± 1.10	O(1)–Mo(2)–S(8)	83.11 ± 1.09
O(2)–Mo(1)–S(1)	114.84 ± 1.06	O(3)–Mo(2)–S(5)	110.23 ± 1.04
O(2)–Mo(1)–S(2)	93.20 ± 1.06	O(3)–Mo(2)–S(6)	98.85 ± 1.03
O(2)–Mo(1)–S(3)	90.04 ± 1.05	O(3)–Mo(2)–S(7)	93.95 ± 1.04
S(3)–Mo(1)–S(4)	67.27 ± 0.37	S(7)–Mo(2)–S(8)	67.40 ± 0.40
S(1)–Mo(1)–S(2)	70.46 ± 0.41	S(5)–Mo(2)–S(6)	70.91 ± 0.41
S(1)–Mo(1)–S(4)	85.55 ± 0.39	S(5)–Mo(2)–S(8)	87.56 ± 0.40
S(2)–Mo(1)–S(4)	81.41 ± 0.38	S(6)–Mo(2)–S(8)	81.13 ± 0.39
S(2)–Mo(1)–S(3)	94.73 ± 0.40	S(6)–Mo(2)–S(7)	92.49 ± 0.43
O(2)–Mo(1)–S(4)	156.07 ± 1.05	O(3)–Mo(2)–S(8)	161.29 ± 1.04
O(1)–Mo(1)–S(2)	158.16 ± 1.11	O(1)–Mo(2)–S(6)	155.93 ± 1.11
S(1)–Mo(1)–S(3)	151.03 ± 0.40	S(5)–Mo(2)–S(7)	152.16 ± 0.45
O(1)–Mo(1)–O(2)	105.32 ± 1.48		
O(1)–Mo(2)–O(3)	102.15 ± 1.45		
Mo(1)–O(1)–Mo(2)	178.03 ± 4.06		

[a] Intervals are standard deviations estimated in the least-squares refinement.

Not included in Table II, but of interest, is the dihedral angle between the $O_1Mo_1O_2$ and $O_3Mo_2O_1$ planes (the angle between the two Mo–O_t bonds projected on a plane perpendicular to Mo–O_b–Mo). This is 4.5 ± 0.5°. The Mo–O_b–Mo group is linear within the limits of significance.

The Mo–S distances vary considerably. The four which are not *trans* to Mo–O bonds are in the range 2.46–2.51 Å., with a mean of 2.487 ± 0.007, which,

(15) In *trans*-$OReCl_3(PEt_2Ph)_2$, H. W. W. Ehrlich and P. G. Owston [*J. Chem. Soc.*, 4368 (1963)] have given 1.60 for the Re–O distance, with no indication of the uncertainty. However, the two-dimensional Fourier method used and the lack of refinement, coupled with the great disparity of the scattering factors for Re and O, render this very uncertain.

(16) F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964).

(17) J. Leciejewicz, Abstracts, 6th International Congress of the International Union of Crystallography, Rome, 1963, No. 4.8.

TABLE III

EQUATIONS OF MOLECULAR PLANES AND DISTANCES OF ATOMS FROM THESE PLANES

A. Planes through the octahedra

1(a) plane through Mo(1), O(1), S(1), S(2), and S(3)

$0.4326X + 0.244Y + 0.868Z = 1.670$

Mo(1)	−0.144	O(1)	0.644
S(1)	0.356	S(2)	−0.544
S(3)	0.299		

1(b) plane through Mo(2), O(1), S(5), S(6), and S(7)

$0.0403X - 0.541Y + 0.840Z = -0.375$

Mo(2)	−0.186	O(1)	0.459
S(5)	0.266	S(6)	−0.241
S(7)	0.303		

2(a) plane through Mo(1), O(1), O(2), S(2), and S(4)

$-0.785X + 0.1104Y + 0.610Z = -1.1636$

Mo(1)	0.0095	O(1)	0.503
O(2)	−0.614	S(2)	0.074
S(4)	−0.044		

2(b) plane through Mo(2), O(1), O(3), S(6), and S(8)

$-0.950X + 0.3113Y + 0.030Z = -0.741$

Mo(2)	0.002	O(1)	−0.563
O(3)	0.491	S(6)	−0.042
S(8)	0.072		

3(a) plane through Mo(1), O(2), S(1), S(3), and S(4)

$0.008X + 0.982Y + 0.1887Z = 0.098$

Mo(1)	0.058	O(2)	−0.326
S(1)	−0.135	S(3)	−0.102
S(4)	0.225		

3(b) plane through Mo(2), O(3), S(5), S(7), and S(8)

$0.097X + 0.943Y + 0.319Z = 4.195$

Mo(2)	−0.078	O(3)	0.069
S(5)	0.156	S(7)	0.182
S(8)	−0.140		

B. The molybdenum xanthate groups

1(a) plane through S(1), S(2), C(1), and O(4)

$0.6346X + 0.019Y + 0.7726Z = 1.962$

S(1)	0.001	C(1)	−0.008
S(2)	0.001	O(4)	0.003
Mo(1)	−0.094		

1(b) plane through S(1), S(2), C(1), O(4), and Mo(1)

$0.6534X + 0.0455Y + 0.7556Z = 1.895$

S(1)	0.020	C(1)	−0.021
S(2)	0.019	O(4)	−0.061
Mo(1)	0.000		

2(a) plane through S(3), S(4), C(2), and O(5)

$-0.197X + 0.9977Y + 0.0645Z = -0.141$

S(3)	0.004	C(2)	−0.058
S(4)	0.004	O(5)	0.026
Mo(1)	0.148		

2(b) plane through S(3), S(4), C(2), O(5), and Mo(1)

$0.0343X + 0.996Y + 0.080Z = 0.129$

S(3)	−0.024	C(2)	−0.041
S(4)	−0.021	O(5)	0.121
Mo(1)	0.000		

3(a) plane through S(5), S(6), C(3), and O(6)

$-0.1744X - 0.4816Y + 0.8599Z = -0.824$

S(5)	0.003	C(3)	−0.029
S(6)	0.003	O(6)	0.011
Mo(2)	0.0745		

3(b) plane through S(5), S(6), C(3), O(6), and Mo(2)

$-0.1517X - 0.4685Y + 0.8703Z = -0.639$

S(5)	−0.013	C(3)	−0.020
S(6)	−0.012	O(6)	0.059
Mo(2)	0.001		

4(a) plane through S(7), S(8), C(4), and O(7)

$0.235X + 0.9166Y + 0.3236Z = 4.238$

S(7)	0.003	C(4)	−0.024
S(8)	0.002	O(7)	0.009
Mo(2)	0.071		

4(b) plane through S(7), S(8), C(4), O(7), and Mo(2)

$0.2186X + 0.9134Y + 0.3433Z = 4.294$

S(7)	−0.012	C(4)	−0.017
S(8)	−0.009	O(7)	0.052
Mo(2)	0.001		

while appreciably longer than the sum of the usual[18] radii (1.04(S) + 1.33(Mo) = 2.37), probably represents a normal Mo^{V}–S bond distance. The particularly interesting fact is that Mo–S bonds which are approximately *trans* to the Mo–O_t bonds are exceptionally long, *viz.*, 2.70 ± 0.01 Å., and even those *trans* to the Mo–O_b bonds are longer, *viz.*, 2.535 ± 0.01, by an amount which is significant. This relative weakness of bonds *trans* to M–O bonds of high multiplicity may be a general phenomenon. Thus $VO(C_5H_7O_2)_2$ exists without any ligand in this position though it will bind various Lewis bases under appropriate conditions. Unfortunately, accurate bond lengths have apparently not been reported for any other molecule in which there are two identical ligands, one *cis* and the other *trans* to an M–O bond of high multiplicity. A precise X-ray study of the $[MoOCl_5]^{2-}$ ion, which is in progress, should provide the required information.

The "best" molecular planes formed by certain groups of atoms and the distances of atoms from these planes were obtained by a least-squares method, using a program written for the IBM 709 computer by J. S. W. The results are given in Table III. The weight, w_i, given to each atom forming the plane was

$$w_i = [\sqrt[3]{(a\sigma_{x_i} b\sigma_{y_i} c\sigma_{z_i})}]^{-2}$$

where the σ_i are the final standard deviations of the atomic coordinates. The orthogonal coordinates, X, Y, Z, in the expressions for the planes are related to the real cell coordinates by the transformations $X_i = ax_i + c \cos \beta z_i$, $Y_i = by_i$, and $Z_i = c \sin \beta z_i$. In part A of Table III, the deviations of atoms from mean planes of the MoO_2S_4 "octahedra" are reported. These deviations are appreciable, but, as noted earlier, the idealization of the structure to two octahedra sharing an apex seems to be a useful approximation.

The Xanthate Groups.—In Table IV, the similarities in the dimensions of the related pairs of xanthate ions are demonstrated and the differences between those of

(18) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 246, 249.

TABLE IV

BOND DISTANCES (Å.) AND INTERBOND ANGLES (DEG.) WITHIN MOLYBDENUM XANTHATE MOIETIES

	Xan-I			Xan-II	
	Mo(1)	Mo(2)		Mo(1)	Mo(2)
a	2.690 ± 0.012	2.715 ± 0.012	*h*	2.458 ± 0.013	2.469 ± 0.013
b	2.509 ± .012	2.508 ± .014	*k*	2.530 ± .013	2.540 ± .013
c	1.562 ± .051	1.558 ± .050	*l*	1.717 ± .046	1.720 ± .045
d	1.713 ± .051	1.723 ± .050	*m*	1.650 ± .046	1.651 ± .045
e	1.389 ± .061	1.405 ± .056	*n*	1.393 ± .052	1.365 ± .052
f	1.475 ± .061	1.460 ± .08	*r*	1.438 ± .060	1.462 ± .066
g	1.509 ± .111	1.502 ± .102	*s*	1.456 ± .082	1.531 ± .075
ab	67.28 ± 0.37	67.40 ± 0.40	*hk*	70.46 ± 0.41	70.91 ± 0.41
ac	83.14 ± 1.87	82.21 ± 1.84	*kl*	84.13 ± 1.57	82.20 ± 1.84
bd	86.27 ± 1.72	85.97 ± 1.69	*hm*	87.87 ± 1.63	86.00 ± 1.69
cd	123.30 ± 3.12	124.42 ± 3.06	*lm*	117.47 ± 2.67	119.05 ± 2.62
ce	122.75 ± 3.71	120.50 ± 3.49	*ln*	119.00 ± 3.11	120.50 ± 3.49
de	113.33 ± 3.44	114.95 ± 3.28	*mn*	123.52 ± 3.22	125.00 ± 3.28
ef	122.54 ± 4.21	122.90 ± 4.02	*nr*	120.56 ± 3.39	123.30 ± 3.57
fg	112.74 ± 5.74	105.20 ± 5.35	*rs*	104.60 ± 4.29	105.60 ± 4.16

one pair and those of the other pair are also displayed. Figure 3 is a sketch of one end of the molecule with the bonds labeled as in Table IV. None of the differences between members of a pair is large enough to be significant, so in discussing the two types of xanthate groups, Xan-I and Xan-II, the average values will be used.

Considering first Xan-I, we note that there is a difference, $a - b$, of 0.20 between the two Mo–S distances. We should then expect there to be a significant difference in the two C–S distances, since the weaker is bond *a*, the closer bond *c* should come to being a double bond and, conversely, the stronger is bond *b*, the closer should bond *d* come to being single. In fact the average value of $d - c$ is 0.16 and this is enough greater than the standard deviations to be significant. From known values[19] for carbon–sulfur bonds, we can estimate the C=S distance to be *ca.* 1.57 Å. and the C—S distance to be *ca.* 1.80 Å. whereas in $KS_2COC_2H_5$, the average C—S distance, corresponding to a bond order of approximately 1.5, is 1.68.[20]

Comparison of these reference values with those found in Xan-I supports the view that bond *c* is of order 1.5–2.0, while bond *d* is of order 1.0–1.5. All the remaining bond lengths in Xan-I are reasonable within their standard deviations. Bond *c* is somewhat short compared to the usual[19] C–O single bond length of 1.43 Å. found in ethers and alcohols, but comparable to that found for the long bonds in carboxylic acids and their esters. Within the significance of the data, no case can be made for any appreciable multiple bonding.

In Xan-II, the bonds *l* and *m* do not differ significantly by Cruickshank's criterion,[21] which is in accord with the fact that bonds *h* and *k* are only slightly, though significantly, different in length. Again, all remaining bond lengths are reasonable.

In all the xanthate groups the sum of the angles about the xanthate-type carbon atom is 360° within the uncertainties, indicating no significant deviation from planarity of the S_2CO group. Also, as shown in Table III, part B, the MoS_2C groups are all essentially planar.

(19) "Tables of Interatomic Distances," Special Publication No. 11, The Chemical Society, London, 1958.

(20) F. Mazzi and C. Tadini, *Z. Krist.*, **118**, 378 (1963).

(21) D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1953).

The Electronic Structure.—Since the molecule lacks any rigorous symmetry elements, a rigorous treatment of its electronic structure would be impracticable. However, by somewhat idealizing the actual geometry, the problem becomes quite tractable and admits of a solution which is neat and satisfying.

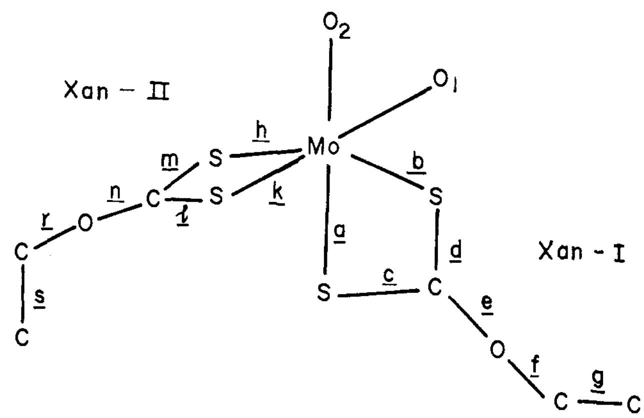

Fig. 3.—A sketch of one end of the molecule identifying bonds in the two types of xanthate groups for reference in Table IV.

We shall assume that the local symmetry of each molybdenum atom is C_{4v}. Let the M–O_t bond define the local *z* axis, and the O_b–Mo–S group define the local *x* (or *y*) axis. We assume now that the $d_{x^2-y^2}$, s, p_x, and p_y orbitals are used to form the four (assumed) coplanar bonds (*b*, *h*, *k*, and Mo–O_b in Fig. 3), and that the p_z and d_{z^2} orbitals are used to form the Mo–O_t σ-bond and to bind the remaining sulfur atom. Finally, following the conclusions of Ballhausen and Gray[22] for the VO^{2+} group, which is isoelectronic with MoO^{3+}, and those of Gray and Hare[23] for $[MoOCl_5]^{2-}$, we assume that the d_{xz} and d_{yz} orbitals are used extensively in forming Mo–O_t π-bonds. Each molybdenum atom now has only one orbital, d_{xy}, which has not yet been used, and this is occupied by one electron.

Turning now to the Mo–O_b–Mo bridge system, we set up a coordinate system as indicated in Fig. 4a. In the center are the p_x and p_y orbitals of oxygen, its p_z and s orbitals having been used to form the Mo–O_b σ-bonds. The unused d-orbitals of the molybdenum atoms, referred to above, are also shown in

(22) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(23) H. B. Gray and C. R. Hare, *ibid.*, **1**, 363 (1962).

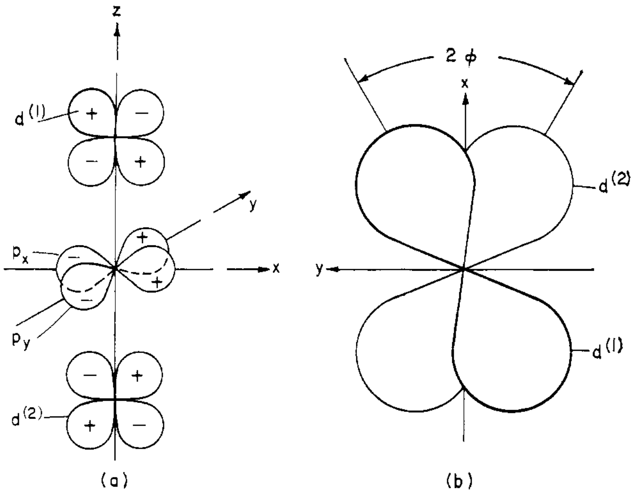

Fig. 4—(a), the coordinate axes and orbitals used in treating the bridge bonding; (b), a sketch showing how the angle of internal twist, ϕ, is defined.

an orientation which is permissible and convenient. In Fig. 4a, these two orbitals are shown as d_{xz} orbitals with reference to the coordinate system for the bridge bonding. However, we know that actually they are not coplanar. Figure 4b shows how we define the noncoplanarity with respect to the x and y axes, using the angle ϕ.

We now regard the orientation, $0 < \phi < \pi/4$, shown in Fig. 4b as the general one; the point symmetry is D_2. In the limiting case where ϕ equals 0, the symmetry is D_{2h}, and in the other limiting case where $\phi = \pi/4$, the symmetry is D_{2d}.

The general case, $0 < \phi < \pi/4$, was treated as follows: the four orbitals, p_x, p_y, $d^{(1)}$, and $d^{(2)}$ span the representations $2b_2 + 2b_3$ of D_2. More particularly, bases for these representations are provided by the following orbitals or combinations

$$b_2\colon\ p_y,\ \frac{1}{\sqrt{2}}\,(d^{(1)} - d^{(2)})$$

$$b_3\colon\ p_x,\ \frac{1}{\sqrt{2}}\,(d^{(1)} + d^{(2)})$$

We now use these as basis functions for a Hückel-type LCAO–MO treatment, leaving ϕ as a free parameter and using the following definitions

$$H_d = \int d^{(1)}\mathcal{H}d^{(1)}\,d\tau = \int d^{(2)}\mathcal{H}d^{(2)}\,d\tau$$

$$H_p = \int p_x\mathcal{H}p_x\,d\tau = \int p_y\mathcal{H}p_y\,d\tau$$

$$H_{dd} = \int d^{(1)}\mathcal{H}d^{(2)}\,d\tau = \int d^{(2)}\mathcal{H}d^{(1)}\,d\tau = 0$$

and

$$H_{dp} = \int d^{(1)}\mathcal{H}p_x\,d\tau = \int d^{(2)}\mathcal{H}p_x\,d\tau$$

when $d^{(1)}$ and $d^{(2)}$ are oriented as shown in Fig. 3a. For a given ϕ, the actual magnitude of the d–p resonance integral will equal H_{dp} multiplied by $\cos\phi$ or $\sin\phi$ as necessary.

The secular equations then take the form

$$b_2\colon\ \begin{vmatrix} H_d - E & (\sqrt{2}\sin\phi)H_{dp} \\ (\sqrt{2}\sin\phi)H_{dp} & H_p - E \end{vmatrix} = 0$$

$$b_3\colon\ \begin{vmatrix} H_d - E & (\sqrt{2}\cos\phi)H_{dp} \\ (\sqrt{2}\cos\phi)H_{dp} & H_p - E \end{vmatrix} = 0$$

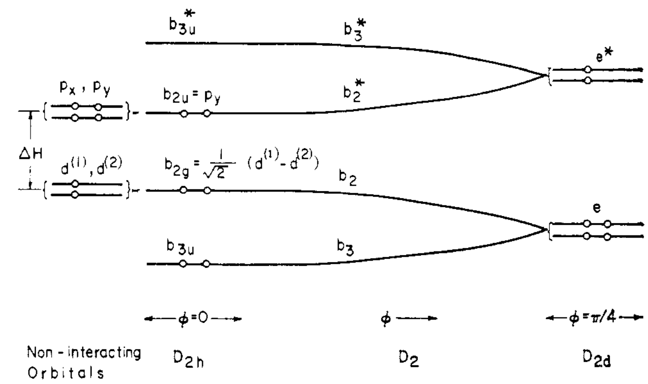

Fig. 5.—An energy level diagram showing the variation of orbital energies and electronic configuration with the angle of internal twist, ϕ.

In the limit of D_{2h} symmetry ($\phi = 0$), the energies of the b_2 orbitals are just H_d and H_p, that is, p_y and $1/\sqrt{2}(d^{(1)} - d^{(2)})$ are nonbonding. Their proper symmetry designations, in D_{2h}, become b_{2g} and b_{2u}, respectively, while p_x and $1/\sqrt{2}(d^{(1)} + d^{(2)})$ both become b_{3u} and their interaction, as given in the b_3 secular equation above, persists. In the limit of D_{2d} symmetry ($\phi = \pi/4$), the p_x and p_y orbitals jointly form a basis for the e representation, as do the combinations $1/\sqrt{2}(d^{(1)} \pm d^{(2)})$. Since $\sin\pi/4 = \cos\pi/4$, the two secular equations become identical. Solving the secular equations for the two special cases and for the general case, the results embodied in Fig. 5 are obtained. Algebraically, the energies of the b_2 and b_3 orbitals are given by

$$2E_{b_2} = \Delta H \pm [(\Delta H)^2 + 8\sin^2\phi(H_{dp})^2]^{1/2}$$

$$2E_{b_3} = \Delta H \pm [(\Delta H)^2 + 8\cos^2\phi(H_{dp})^2]^{1/2}$$

It has been assumed that the metal d orbitals are more stable than the oxygen p orbitals, as is generally the case. The opposite assumption would not alter the pattern of molecular orbital energies, but only change their fractions of d and p character.

It can now be seen that on the basis of orbital energies alone, the D_{2h} configuration is favored, but there will be a more favorable exchange energy in the D_{2d} configuration. There will also be repulsions between sulfur atoms and the two O_t atoms, which will presumably tend to favor the D_{2d} configuration. Finally, in the crystal, intermolecular forces may influence the configuration.

Our X-ray investigation shows that the balance of these various forces is such as to give a ϕ of *ca.* 2.25° and from the fact that the compound is diamagnetic, we know that this is less than ϕ^*, the critical value beyond which a triplet ground state would become stabilized. It should be noted that the energies of the various orbitals vary with ϕ according to $\cos^2\phi$ and $\sin^2\phi$; that is for small ϕ, they are rather insensitive to ϕ, so it may well be that ϕ^* is quite a bit larger than the value of ϕ observed in the crystal. It is also possible that, when free of intermolecular constraints, the molecule might have an appreciably larger value of ϕ and still be diamagnetic.

In view of the results of the above analysis, we might conclude that in some similar cases, if not in this one, the energy difference between singlet ($\phi < \phi^*$) and triplet ($\phi > \phi^*$) species might be so small as to be of the order of thermal energies. Thus a Boltzmann distribution could exist between the two. In this way, one might explain the reported existence[24] of both singlet and triplet binuclear Mo(V) species in hydrochloric acid solutions of Mo(V). Both would have the general constitution $[Cl_4Mo(O){-}O{-}Mo(O)Cl_4]^{4-}$.

(24) C. R. Hare, I. Bernal, and H. B. Gray, *Inorg. Chem.*, **1**, 831 (1962).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, PRINCETON UNIVERSITY, PRINCETON, NEW JERSEY]

Isotropic Proton Magnetic Resonance Shifts in π-Bonding Ligands Coordinated to Paramagnetic Nickel(II) and Cobalt(II) Acetylacetonates

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Isotropic proton magnetic resonance shifts due to contact and pseudo-contact interactions have been observed for protons in certain triarylphosphines and isonitrile molecules when these are placed in solution in $CDCl_3$ with the paramagnetic Ni(II) and Co(II) acetylacetonates. The alternation in sign of the observed shifts for adjacent protons on the phenyl rings is evidence for delocalization of spin density into the π-orbitals of these ligands when coordinated to both Co(II) and Ni(II) acetylacetonates. Evidence for a large upfield pseudo-contact shift in the cobalt systems is presented. Proton spin–spin coupling constants for the arylphosphines and isonitriles are given.

Introduction

This paper reports a high resolution proton magnetic resonance (p.m.r.) study of interactions in solution between π-bonding ligands and the paramagnetic chelates, cobalt(II) and nickel(II) acetylacetonate [bis(2,4-pentanediono)cobalt(II) and -nickel(II)], hereafter referred to as $Co(AA)_2$ and $Ni(AA)_2$. Large, concentration-dependent chemical shifts from the values in the diamagnetic ligands are observed for the proton resonances of certain triarylphosphines and isonitrile molecules when these are placed in chloroform solution with the paramagnetic complexes.

A great deal of extremely detailed and fundamental knowledge about the electronic structure of certain paramagnetic systems can be obtained from their p.m.r. spectra. The elegant work of Phillips and his co-workers[1–5] on the Ni(II)aminotroponeimineates and related systems illustrates the potential of this technique. Most of the recent work in this field has been confined to systems containing Ni(II); however, recently several studies of systems containing Co(II) have appeared.[6–9] Of particular interest to this work is the investigation by Happe and Ward[8] of the p.m.r. spectra of pyridine-type bases complexed with $Ni(AA)_2$ and $Co(AA)_2$.

The theory of isotropic nuclear resonance shifts has been discussed at length by McConnell and Robertson.[10] The conditions necessary for the observation of proton resonances in paramagnetic systems are by now well established.[2,10,11] Either the electronic spin-lattice relaxation time, T_1, or a characteristic electronic exchange time, T_e, must be short compared with the isotropic hyperfine contact interaction constant, A_i, in order for resonances to be observed.

The contact interaction gives rise to a shift in resonance from the diamagnetic position due to the presence of unpaired spin density at the resonating nucleus. This spin density can be transmitted through the ligands by either σ- or π-orbitals. Another possible cause of an isotropic nuclear resonance shift is the pseudo-contact interaction which arises from anisotropy in the *g*-tensor of the paramagnetic complex. The pseudo-contact shift for a given proton depends on its geometrical position in the molecule.[10,12,13]

The shifts observed in the Ni(II) aminotroponeimineates have been satisfactorily explained by assuming that the unpaired electron spin density is distributed *via* the π-orbitals of these unsaturated ligands. Spin density in the σ-orbitals and the pseudo-contact interaction are apparently unimportant in these systems.[1–5] Happe and Ward interpreted the resonance shifts in pyridine-type ligands coordinated to $Ni(AA)_2$ as being due to spin density being transferred *via* the σ-orbitals. In the case of the $Co(AA)_2$–pyridine-type base complexes, they found that a pseudo-contact interaction contributes significantly to the observed shifts as well.

The spectra of labile complexes, such as adducts of $Co(AA)_2$ or $Ni(AA)_2$, exhibit a time average spectrum.[8] If the exchange of ligands between complexed and uncomplexed sites is rapid compared with the separation in resonance frequency for a given proton in the paramagnetic and diamagnetic environments, the various proton resonances will be shifted from their normal diamagnetic values by an amount proportional to the shifts in the complexes. Also, the more diamagnetic ligand is added to the system, the smaller become the observed shifts. Since the shifts we have observed are as large as 500 c.p.s., the rate at which this ligand exchange occurs must be in excess of 10^3 sec.$^{-1}$.

Noting that the results of Happe and Ward indicate that spin density is transferred only through the σ-

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