and the aluminum atom. If the gallium–phosphine system is analogous to this, nine methyl groups would be reasonably close to each other in the transition state illustrated in eq 4. Since this is not energetically favorable, the reaction proceeds through the dissociative mechanism.

Correspondence

Solid-State Behavior of Some Cobalt(II) Complexes Containing Trimethylamine N-Oxide

Sir:

Recently[1] we reported the preparation and study of several $Co(TMNO)_2X_2$ (TMNO = trimethylamine N-oxide; X = halide, NCS) complexes. While the solution behavior of these complexes, alone and in the presence of added base, was easily interpreted by assuming a constant coordination number of 4 for the cobalt(II) ion, the solid-state data defied such interpretation. Definite differences between solid and solution electronic spectra were noted (Figures 1 and 2), and attempts to calculate values of λ' using solid-state moments (Table I) and solution-state spectrochemical data[1] gave completely unreliable results. Thus the use of a tetrahedral (or pseudotetrahedral) model for the crystalline compounds was discarded, although nothing definite was then formulated regarding their structures.

While the electronic spectra of these complexes are quite different from those in pseudooctahedral cases, such as $Co(C_5H_5N)_2Cl_2$,[2] they do compare quite favorably with those of several complexes (such as $[Co(Me_6tren)Br]Br$,[3] $Co(Et_4dien)Cl_2$,[4] $Co(Me_5dien)Cl_2$,[5] and $[Co((C_6H_5)_2CH_3AsO)_4(ClO_4)]ClO_4$[6]) known from X-ray studies to contain pentacoordinated cobalt(II). Thus it seems that these crystalline $Co(TMNO)_2X_2$ complexes do not contain four- but rather five-coordinate cobalt(II).

The achievement of pentacoordination in these complexes requires that some type of ligand bridging be occurring, thereby reducing the molecular symmetry to a rather low level. Thus these complexes will be best described as having either distorted trigonal-bipyramidal or distorted square-pyramidal structures. While it has been noted that the pattern of allowed electronic transitions for pentacoordinate cobalt(II) complexes is relatively independent of structure,[3a,4a,7] these compounds do not possess the characteristics needed for stabilizing a square-pyramidal structure[8] and thus are probably more closely trigonal bipyramidal in nature.

Using the idealized C_{3v} symmetry point group[3a] for these complexes, the assignments for the electronic transitions can be made as follows: ν_2, $^4A_2(F) \rightarrow {}^4E(F)$; ν_3, $^4A_2(F) \rightarrow {}^4E(F)$; ν_4, $^4A_2(F) \rightarrow {}^4A_2(P)$; ν_5, $^4A_2(F) \rightarrow {}^4E(P)$. An alternative set of assignments, in which the ν_3 band would be assigned as a spin-forbidden transition (in D_{3h} symmetry),[9] does not appear feasible if the widths of the spin-allowed and spin-forbidden bands are compared (Figure 2). The general positions of the main transitions and the magnetic moments vary in the anticipated way. The strengths of the ligand fields in these complexes (as determined by the transition energies) appear to be greater than those of the $Co(Et_4dien)X_2$[4a] and $Co(Me_5dien)X_2$[5a] complexes and approximately equal to those of the $[Co(Me_6tren)X]X$[3b] complexes. These findings are consistent with the high donor strength for TMNO found in four-coordinated cobalt(II) complexes.[1]

Determination of the identity of the bridging ligands is complicated by the fact that the metal ions, anions, and amine oxides[10] are all capable of such behavior. Metal–metal interaction appears unlikely, however, in light of the high magnetic moments recorded for the complexes (Table I). While it is apparent from the electronic spectra that the three halide complexes (and probably the thiocyanate complex) have the same structure, it is unfortunate that no physical method other than X-ray diffraction (or possibly nuclear quadrupole resonance) can definitively ascertain the nature of the bridging species in the halide complexes.

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(1) D. W. Herlocker and R. S. Drago, *Inorg. Chem.*, **7**, 1479 (1968).

(2) N. S. Gill, R. S. Nyholm, G. A. Barclay, T. I. Christie, and P. J. Pauling, *J. Inorg. Nucl. Chem.*, **18**, 88 (1961).

(3) (a) M. Ciampolini and I. Bertini, *J. Chem. Soc., A*, 2241 (1968); (b) M. Ciampolini and N. Nardi, *Inorg. Chem.*, **5**, 41 (1966); (c) M. Ciampolini, N. Nardi, and G. P. Speroni, *Coord. Chem. Rev.*, **1**, 222 (1966); (d) M. Di Vaira and P. L. Orioli, *Inorg. Chem.*, **6**, 955 (1967); $Me_6tren = N[CH_2CH_2N(CH_3)_2]$.

(4) (a) Z. Dori and H. B. Gray, *ibid.*, **7**, 889 (1968); (b) Z. Dori and H. B. Gray, *J. Am. Chem. Soc.*, **88**, 1394 (1966); (c) Z. Dori, R. Eisenberg, and H. B. Gray, *Inorg. Chem.*, **6**, 483 (1967); $Et_4dien = HN[CH_2CH_2N(CH_2CH_3)_2]_2$.

(5) (a) M. Ciampolini and G. P. Speroni, *ibid.*, **5**, 45 (1966); (b) M. Di Vaira and P. L. Orioli, *Chem. Commun.*, 590 (1965); $Me_5dien = CH_3N[CH_2CH_2N(CH_3)_2]_2$.

(6) (a) J. Lewis, R. S. Nyholm, and G. A. Rodley, *Nature*, **207**, 72 (1965); (b) P. Pauling, G. B. Robertson, and G. A. Rodley, *ibid.*, **207**, 73 (1965).

(7) C. Furlani, *Coord. Chem. Rev.*, **3**, 141 (1968).

(8) Furlani states that a square-pyramidal structure can possibly be stabilized if any one or a combination of the following factors is present: (a) a ligand system (such as a pentadentate Schiff's base) which imposes the geometry upon the metal ion; (b) a weak, often electrostatic, interaction between a square-planar complex and a fifth ligand, as found in some palladium(II) complexes; and (c) the loss of stabilizing π bonding if the five-coordinate species were to distort from square-pyramidal geometry. These cobalt complexes possess none of the above qualities, and in addition the presence of unidentate, electronegative ligands is a factor which favors trigonal-bipyramidal coordination of metal ions.[7]

(9) J. S. Woods, *Inorg. Chem.*, **7**, 852 (1968).

(10) Thus pyridine N-oxide (C_5H_5NO) has been shown[11,12] to act as a bridge between the two copper atoms in dimeric $[Cu(C_5H_5NO)Cl_2]_2$.

(11) H. L. Schäfer, J. C. Morrow, and H. M. Smith, *J. Chem. Phys.*, **42**, 504 (1965).

(12) R. S. Sager, R. J. Williams, and W. H. Watson, *Inorg. Chem.*, **6**, 951 (1967).

TABLE I

ELECTRONIC SPECTRAL DATA (CM^{-1}) FOR THE $Co(TMNO)_2X_2$ COMPLEXES

X	ν_2[a]	ν_3	ν_4	ν_5	Others[b]	μ, BM[c]
Cl	7905	14,390	[16,130, 16,720][d]	18,870	23,260	4.71
Br	7940	13,990	16,720	19,230	16,000, 17,950, 23,200	4.77
I	7460	13,300	15,950	19,230	15,360, 17,090, 22,620	4.88
NCS	[7220, 8100][d]	15,220	17,060	20,200	. . .	4.54

[a] The energy scheme used here is that of M. Ciampolini and I. Bertini, *J. Chem. Soc., A*, 2241 (1968). For assignments, see text. [b] Spin-forbidden bands. [c] Data taken from ref 1. [d] These peaks are part of a doublet. The peak at 16,130 cm^{-1} may be a spin-forbidden band which has gained intensity from the transition at 16,720 cm^{-1}.

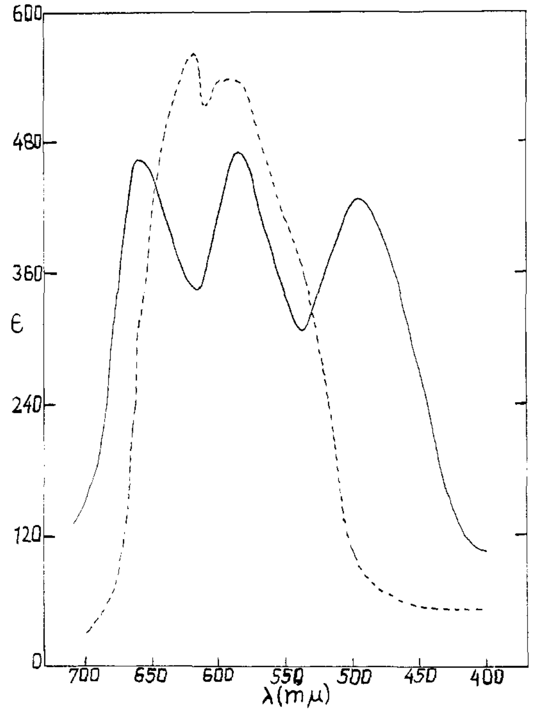

Figure 1.—Electronic spectra in the visible region for $Co(TMNO)_2(NCS)_2$ dissolved in acetonitrile (- - -) and in the solid state (—) (ϵ values are arbitrary for the solid state).

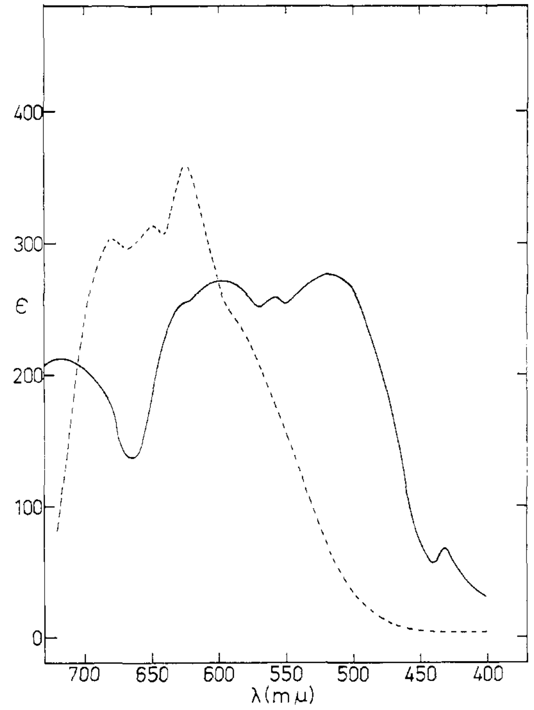

Figure 2.—Electronic spectra in the visible region for $Co(TMNO)_2Br_2$ dissolved in acetonitrile (- - -) and in the solid state (—) (ϵ values are arbitrary for the solid state).

Thus it has already been noted[13,14] that no meaningful information can be obtained from infrared spectroscopy regarding metal–oxygen interactions in TMNO complexes. The existence of two metal–halogen infrared stretching frequencies (originally interpreted as evidence for the pseudotetrahedral nature of the $Co(TMNO)_2(\text{halide})_2$ complexes[15]) could arise from the low symmetry of the complex and/or the dissimilarity of the halide ions (one bridging and one terminal). A preliminary X-ray study of the structure of $Co(TMNO)_2Br_2$ has shown only that molecular association appears to be present,[16] a result consistent with that obtained from the electronic spectral data.

Examination of the C–N and C–S stretching frequencies in the thiocyanate complex does, however, offer some insight into this matter. These vibrations are found at 2075 and 824 cm^{-1}, respectively, within the normal ranges expected for the terminally nitrogen-bonded species[17] and similar to those found for $[Co(HMPA)_2(NCS)_2]$ (2083 and 835 cm^{-1}), known to contain only terminally nitrogen-bonded thiocyanate groups.[18] In addition, the sharpness of the C–N stretching vibration contrasts with the broad band found at approximately 2100 cm^{-1} in several complexes thought to contain both bridging and terminal thiocyanate groups.[19,20] Since the spectra of both $Co(TMNO)_2(NCS)_2$ and $Co(TMNO)_2Br_2$ are identical in the 700–800-cm^{-1} region (one Nujol band and the symmetric C–N stretch in the TMNO moiety[21]), it seems quite apparent that there are no bridging thiocyanate ions in this complex.

The nature of the coordination sphere about the

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(13) R. S. Drago, J. T. Donoghue, and D. W. Herlocker, *Inorg. Chem.*, **4**, 836 (1965).

(14) S. Kida, *Bull. Chem. Soc. Japan*, **36**, 712 (1963).

(15) S. M. Hunter, V. M. Langford, G. A. Rodley, and C. J. Wilkins, *J. Chem. Soc., A*, 305 (1968).

(16) G. A. Rodley, personal communication, University of Canterbury, Christchurch, New Zealand, 1968.

(17) J. L. Burmeister, *Coord. Chem. Rev.*, **3**, 225 (1968).

(18) J. T. Donoghue and R. S. Drago, *Inorg. Chem.*, **2**, 572 (1963).

(19) (a) L. Sacconi, R. Morassi, and S. Midollini, *J. Chem. Soc., A*, 1510 (1968). (b) While the C–N stretching frequency for bridging thiocyanate groups is listed by Burmeister[17] as $\gtrsim 2140$ cm^{-1}, there are a number of cases[20] in which compounds known to contain bridging thiocyanate groups possess a C–N stretching frequency of 2090–2110 cm^{-1}. Thus the comparison of the infrared spectra of $Co(TMNO)_2(NCS)_2$ and the compounds of Sacconi, *et al.*,[19a] indicates a definite difference in the mode of ligand bonding in these two instances.

(20) See, for example, S. M. Nelson and T. M. Shepherd, *J. Inorg. Nucl. Chem.*, **27**, 2123 (1965).

(21) P. A. Giguère and D. Chin, *Can. J. Chem.*, **39**, 1214 (1961).

cobalt ion in the thiocyanate complex (and quite likely the halide complexes) is thus CoO_3X_2. The strength of the bridging bonds is not excessive, since they break easily as the compound dissolves in dichloromethane and acetonitrile.[1] Since structures consistent with the observed stoichiometry could involve dimers, trimers, or heavier moieties, the exact stereochemistry can probably be determined only by X-ray diffraction.

[22] Most of the experimental work reported herein was performed at the University of Illinois and is abstracted from the Ph.D. thesis of D. W. Herlocker.

DEPARTMENT OF CHEMISTRY
WESTERN MARYLAND COLLEGE[22]
WESTMINSTER, MARYLAND 21157
DAVID W. HERLOCKER

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Variation of the Oxygen Positional Parameter in Pyrochlores

Sir:

In a recent article Sleight[1] reported on three ternary oxides of mercury with the composition $A_2B_2O_7$ and the pyrochlore-type structure (space group Fd3m). He discussed the several possible choices of origin in the pyrochlore cell and listed (his Table IV) values of the oxygen positional parameter and metal–oxygen bond lengths which have been reported for 12 compounds. The observed range in the oxygen parameter, x = 0.305–0.355,[2] is stated to be "significantly different from an incorrect range (x = 0.325–0.355) recently given by Hoekstra and Siegel."[3]

The difference in x may possibly be considered significant, since the amended range includes the value x = 0.3125 in which regular octahedra are formed about the B atoms of $A_2B_2O_7$, but it is not due to an "indiscriminate use of x parameters from various pyrochlores where different origins were used" as Sleight suggests. Of the 12 compounds listed in his Table IV two, $Cd_2Re_2O_7$[4] and $Cd_2Nb_2O_7$, have x parameters less than 0.3125, and the error limits given on $Cd_2Re_2O_7$ could put it on either side of the regular octahedral configuration. Cadmium niobate was studied by Jona, Shirane, and Pepinsky[5] and given an x parameter of 0.305 ± 0.003. Sleight indicated that this value was obtained with niobium at the origin of the unit cell. While Jona, *et al.*, made no definitive statement on this point, we believe that all evidence points to the fact that these authors placed O_I at the origin.

(1) Figure 2 of Jona, *et al.*,[5] illustrates the pyrochlore structure projected on the (110) plane. The legend refers to Nb and Cd ions at $(^1/_8, ^1/_8)$ positions. The metal ions are found at these locations only with O_I at the origin.

(2) In section IV (p 906) Jona, *et al.*,[5] reported that "general intensity relations can be explained very well by Cd and Nb positions as given by Bystroem." Bystroem[6] placed O_I at the origin.

(3) Bond lengths and ionic radii calculated with $x = 0.305$ and O_I at the origin are more reasonable than with B atoms at the origin. Niobium and tantalum are generally considered to have virtually identical ionic radii. (In fact, Sleight made this assumption in his compounds, $Hg_2Nb_2O_7$ and $Hg_2Ta_2O_7$.) Bond lengths calculated for $Cd_2Nb_2O_7$ with $x = 0.305$ and niobium at the origin are Nb–O_{II} = 1.92 Å and Cd–O_{II} = 2.73 Å (not 2.67 Å as given by Sleight[1]). However, with $x = 0.320$ the bond lengths are Nb–O_{II} = 1.97 Å and Cd–O_{II} − 2.62 Å. Recent data for $Cd_2Ta_2O_7$ with $x = 0.317$ give Ta–O_{II} = 1.96 Å and Cd–O_{II} = 2.64 Å. It is apparent that significantly better agreement in calculated bond lengths is obtained with O_I at the origin. For these reasons we believe that the correct value for x in $Cd_2Nb_2O_7$ is 0.320 based on B_0 as the origin and that only $Cd_2Re_2O_7$ requires any appreciable extension of the range in x beyond the approximate range given in our paper. We wish to emphasize, however, that new data may require a further revision in x sometime in the future.

[1] A. W. Sleight, *Inorg. Chem.*, **7**, 1704 (1968).

[2] For the purposes of the following discussion, we will adopt Sleight's choice of origin (B_0).

[3] H. R. Hoekstra and S. Siegel, *Inorg. Chem.*, **7**, 141 (1968).

[4] P. C. Donahue, J. M. Longo, R. D. Rosenstein, and L. Katz, *ibid.*, **4**, 1152 (1965).

[5] F. Jona, G. Shirane, and R. Pepinsky, *Phys. Rev.*, **98**, 903 (1955).

[6] A. Bystroem, *Arkiv. Kemi Mineral. Geol.*, **18A**, No. 21 (1944).

CHEMISTRY DIVISION
ARGONNE NATIONAL LABORATORY
ARGONNE, ILLINOIS 60439
HENRY R. HOEKSTRA
STANLEY SIEGEL

RECEIVED DECEMBER 26, 1968

Reply to: "Variation of the Oxygen Positional Parameter in Pyrochlores"

Sir:

Recently I have disagreed with Hoekstra and Siegel (HS) concerning the range of the oxygen parameter in the pyrochlore structure.[1,2] Two examples of compounds ($Cd_2Nb_2O_7$ and $Cd_2Re_2O_7$) were given where the oxygen parameters were outside the range given by HS. In reply to HS,[3] I agree that it is very likely that the oxygen parameter for $Cd_2Nb_2O_7$ actually falls within the range that they had given. This means that the origin chosen by HS is not a center of symmetry, and although it seems preferable to choose the origin at a center of symmetry for a centrosymmetric structure, this practice has frequently not been followed for the pyrochlore structure.

In the case of $Cd_2Re_2O_7$ the origin was specifically stated;[4] thus, the range of the oxygen positional

[1] A. W. Sleight, *Inorg. Chem.*, **7**, 1704 (1968).

[2] H. R. Hoekstra and S. Siegel, *ibid.*, **7**, 141 (1968).

[3] H. R. Hoekstra and S. Siegel, *ibid.*, **8**, 2039 (1969).

[4] P. C. Donohue, J. M. Longo, R. D. Rosenstein, and L. Katz, *ibid.*, **4**, 1152 (1965).