imines should approximate analogous complexes with ligands containing the α-diimine arrangement. In contrast, if the electron pair is localized on the sulfur atom, thus precluding conjugation, the Dq values for these complexes should be significantly lower. A study of the electronic spectra of the nickel complexes (Table II) shows that there is a large decrease in the value for the splitting parameter when an ethylidene, or other such groups (ES, PS, and BS complex), is substituted for the pyridinal array (TPPI complex). This difference demonstrates that the electron pair is localized on the sulfur atom and does not enter into appreciable conjugation with the rest of the molecule.

The final group of complexes to be discussed results from the reaction of metal perchlorates with N(2-thiopyridine 1-oxide)2-pyridinalimine. This ligand coordinates in a tridentate manner. In addition to the two imine nitrogens coordination also takes place through the N-oxide group. This is supported by infrared spectra, which indicate that the N-oxide stretching frequency is shifted to longer wave lengths for the complexes as compared to the free ligand (Table III), a behavior consistent with that reported for similar N-oxide complexes.[8,9] This behavior is explained as arising from a decrease in the double-bond character of the N–O bond upon coordination.[10]

One additional point is noteworthy. The iron(II) complex is high-spin, a behavior that is rather unusual with ligands containing the α-diimine array. The alteration in the spin multiplicity of this species as compared to the other α-diimine-containing complexes reported herein resides in the nature of the third coordinating atom. In contrast to N(2-thiopyridine)-2-pyridinalimine where chelation occurs through three imine atoms, coordination in N(2-thiopyridine 1-oxide)2-pyridinalimine is through one oxygen and two nitrogen atoms. Therefore, the alteration in properties evolves itself to a difference in the metal–ligand interaction of a pyridine nitrogen atom as contrasted to a N-oxide atom. This alteration is dramatized by the large decrease in the value for the splitting parameter of the nickel complexes of the two ligands. Placing an oxide atom on the pyridine nitrogen results in a decrease in the Dq value from 1235 to 980 cm.$^{-1}$. This is consistant with the decrease in the Dq value for the hexapyridinenickel(II) ion as compared to the (hexapyridine N-oxide)nickel(II) ion (1015 cm.$^{-1}$ *vs.* 840 cm.$^{-1}$)[11] as well as the tris(bipyridyl)nickel(II) ion as contrasted to the tris(bipyridyl di-N-oxide)nickel(II) ion, where the Dq value drops from 1150 to 857 cm.$^{-1}$.[11]

Acknowledgment.—We wish to acknowledge the microanalytical group at Olin Mathieson, who expertly handled and analyzed the explosive samples reported herein.

---

[8] A. Vinciguerra, P. G. Simpson, Y. Kakiuti, and J. V. Quagliano, *Inorg. Chem.*, **2**, 286 (1963).

[9] J. V. Quagliano, J. Fujita, G. Franz, D. J. Walmsley, and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).

[10] S. Kida, J. V. Quagliano, S. A. Walmsley, and S. Y. Tyree, *Spectrochim. Acta*, **19**, 189 (1963).

[11] S. K. Madan and W. E. Bull, *J. Inorg. Nucl. Chem.*, **26**, 2211 (1964).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CASE INSTITUTE OF TECHNOLOGY, CLEVELAND, OHIO 44106

Preparations and Properties of Chromium(II) Complexes.
III. Complexes with Dimethyl Sulfoxide[1]

BY DAVID G. HOLAH AND JOHN P. FACKLER, JR.

Received July 9, 1965

Dimethyl sulfoxide (DMSO) complexes of chromium(II) halides have been prepared. These complexes have the stoichiometries $CrCl_2 \cdot 2DMSO$, $CrBr_2 \cdot 3DMSO$, and $CrI_2 \cdot 4DMSO$, but all appear from their visible reflectance spectra to contain six-coordinate, *i.e.*, distorted octahedral, chromium(II). In view of the similarity of chromium(II) and copper(II) chemistry, the DMSO complexes of copper(II) halides have been re-examined and have been found not to contain CuX_4^{2-} as was previously suggested. The complexes $CuCl_2 \cdot 2DMSO$, $CuBr_2 \cdot 2DMSO$, and $CrCl_2 \cdot 2DMSO$ appear to be isomorphous and have similar infrared spectra. The chromium(II) complexes display normal high-spin room temperature magnetic susceptibilities.

Introduction

Since 1960 a large number of dimethyl sulfoxide (DMSO) complexes of first row transition metal salts have been prepared and characterized.[2–8] The ligating properties of DMSO have been discussed and the position of the ligand in the spectrochemical[7] and nephelauxetic[9] series has been established. To our knowledge none of these studies has included work on

---

[1] Part II: D. G. Holah and J. P. Fackler, Jr., *Inorg. Chem.*, **4**, 1112 (1965).

[2] H. L. Schläfer and W. Schaffernicht, *Angew. Chem.*, **72**, 618 (1960).

[3] F. A. Cotton and R. Francis, *J. Am. Chem. Soc.*, **82**, 2986 (1960).

[4] D. W. Meek, D. K. Straub, and R. S. Drago, *ibid.* **82**, 6013 (1960).

[5] F. A. Cotton, R. Francis, and W. D. Horrocks, Jr., *J. Phys. Chem.*, **64**, 1534 (1960).

[6] F. A. Cotton and R. Francis, *J. Inorg. Nucl. Chem.*, **17**, 62 (1961).

[7] H. L. Schläfer and H. P. Opitz, *Z. Elektrochem.*, **65**, 372 (1961).

[8] J. Selbin, W. E. Bull, and L. H. Holmes, *J. Inorg. Nucl. Chem.*, **16**, 219 (1961).

[9] D. W. Meek, R. S. Drago, and T. S. Piper, *Inorg. Chem.*, **1**, 286 (1962).

chromium(II). However, it is now well known[1,10,11] that chromium(II) and copper(II) form similar compounds, and reports of several DMSO complexes of the latter metal have appeared in the recent literature.

The complexes $CuX_2 \cdot 2DMSO$, X = Cl and Br, appear to be the most stable[2–4,8] of the copper(II) halide–DMSO series, although $CuCl_2 \cdot DMSO$[8] and $CuBr_2 \cdot 3DMSO$[2,3] also exist; the latter complex, in which one DMSO molecule is only weakly held, readily reverts to $CuBr_2 \cdot 2DMSO$ when allowed to stand in air.[3] Infrared spectra in the S=O stretching region have been used extensively[4,5,8,12] to show that in the great majority of the complexes, including those of copper(II), the DMSO is bonded to the metal *via* the oxygen atom. However, there remains some disagreement regarding the assignment[12] of certain infrared bands.

There are also conflicting statements regarding the structures of the bis(dimethyl sulfoxide)copper(II) halides. Selbin, *et al.*,[8] suggest an essentially planar monomeric unit $[CuX_2 \cdot 2DMSO]$, but point out that in the solid state the coordination number of the copper may be greater than four. Drago and co-workers[4,12] formulate the complexes as dimeric units, $[Cu(DMSO)_4][CuX_4]$, and suggest that the CuX_4^{2-} anion is tetrahedral, at least in solution,[4] although they advance no strong evidence for this conclusion.

Continuing our studies of chromium(II) chemistry,[1,11] we have prepared complexes of chromium(II) halides with DMSO and examined some of their physical properties. We also have reinvestigated the complexes formed from copper(II) halides and DMSO and have compared the structures and spectra of these materials with corresponding properties of the chromium(II) complexes. The possibility of isolating a tetrahedral chromium(II) complex prompted certain aspects of this work.

Experimental

All experiments were carried out under a nitrogen atmosphere in equipment previously described.[11]

Chromium(II) halides,[11] hydrated or anhydrous, dissolve in DMSO to give dark green solutions. Much of the DMSO is removed under vacuum. Pale blue crystals form which are filtered off and recrystallized from 100% ethanol. Analyses are shown in Table I. Considerable quantities of insoluble, fine green impurities are formed in the DMSO bromide and (particularly) iodide solutions but if, during recrystallization, the hot ethanol solutions are filtered through a fine porosity sinter and the product isolated as quickly as possible, the impurities can be eliminated. The bromide and iodide complexes redissolve in ethanol or DMSO to form cloudy solutions.

A blue-green solid was isolated from the reaction of $Cr(ClO_4)_2 \cdot 6H_2O$ with DMSO. This solid exploded with great violence during attempts to recrystallize it from ethanol.

The complexes $CuCl_2 \cdot 2DMSO$, $CuBr_2 \cdot 2DMSO$, and $CuBr_2 \cdot 3DMSO$ were prepared as previously described[3] and recrystallized from ethanol. Carbon and hydrogen analyses were in excellent agreement with the theoretical values for these complexes. The longer preparative method described by Meek, *et al.*,[4] is not required.

Physical measurements were carried out as previously described.[1,11] Infrared spectra of KBr disks and Nujol mulls were recorded on a Beckman Model IR-8 spectrophotometer.

Table I

Analyses and Magnetic Data

		Analyses, %				Magnetic moments[b] (at 20°)	
		Cr[a]	X[a]	C	H	$\chi_g \times 10^6$	μ_{eff}, cor., B.M.
$CrCl_2 \cdot 2DMSO$	Calcd.	18.63	25.40	17.21	4.33	36.2	4.91
	Found	19.0	25.2	17.1	4.3		
$CrBr_2 \cdot 3DMSO$	Calcd.	11.66	35.82	16.15	4.07	22.8	4.96
	Found	11.7	35.5	16.7	4.2		
$CrI_2 \cdot 4DMSO$	Calcd.	8.41	41.05	15.54	3.91	16.35	4.95
	Found	8.4	41.0	15.5	3.9		

[a] See part I[11] for method of analysis. [b] Diamaghetic corrections obtained as in part I.[11]

Results

Infrared spectra of the compounds in the region of the S=O stretch are complex. The bands between 900 and 1250 cm.$^{-1}$ are shown in Figure 1. The spectra of all the complexes studied, including $CuBr_2 \cdot 3DMSO$, are blank in the 1050 cm.$^{-1}$ region, where the free S=O stretch in liquid DMSO occurs.[5] The spectra are also blank in the 1100–1120 cm.$^{-1}$ region, where the S=O stretch is reported to occur[5] when DMSO is coordinated *via* the S atom. It seems certain therefore that all the DMSO in these complexes is bonded to the metal atoms through the oxygen. The strongest and broadest bands in the spectra appear in the 900–950 cm.$^{-1}$ region. Changes in the detail of the bands in this region occur through the series of complexes studied. The sharp bands between 950 and 1150 cm.$^{-1}$, however, do not move to any perceptible extent, although the resolution is not the same for each complex. Note the similarity (Figure 1) between the spectra of the compounds $CrCl_2 \cdot 2DMSO$, $CuCl_2 \cdot 2DMSO$, and $CuBr_2 \cdot 2DMSO$. Note also that the spectra of $CuBr_2 \cdot 3DMSO$ and $CrBr_2 \cdot 3DMSO$ are similar but slightly different from those of the other complexes.

The magnetic moments of the chromium(II) halide–DMSO complexes studied are included in Table I and are normal for high-spin $3d^4$ systems.

Reflectance spectra are shown in Table II and Figure 2. The spectra of $CrCl_2 \cdot 2DMSO$ and $CrBr_2 \cdot 3DMSO$ differ considerably from those of the bis(pyridine)[1] and bis(acetonitrile)[13] complexes. The bands here are not distinctly doubled but are extremely broad, with asymmetry on the high-energy side (Figure 2) and half-widths between 6000 and 7000 cm.$^{-1}$. At 77°K. a weak shoulder appears at 8500 cm.$^{-1}$ in $CrCl_2 \cdot 2DMSO$, along with several weak bands on the high-energy side of the main absorption. At low temperatures $CrI_2 \cdot 4DMSO$ (Figure 1) has a spectrum which clearly shows the presence of two components as observed in the spectra of other chromium(II) complexes. Reflectance spectra of $CuX_2 \cdot 2DMSO$ (X = Cl, Br), reported here for the first time, are also recorded in Table II and are very similar to their chromium(II) analogs in intensity, position, and shape of the bands. Room and low temperature reflectance

---

[10] H. Lux, L. Eberle, and D. Sarre, *Chem. Ber.*, **97**, 503 (1964).

[11] J. P. Fackler, Jr., and D. G. Holah, *Inorg. Chem.*, **4**, 954 (1965).

[12] R. S. Drago and D. W. Meek, *J. Phys. Chem.*, **65**, 1446 (1961).

[13] D. G. Holah and J. P. Fackler, Jr., *Inorg. Chem.*, to be published.

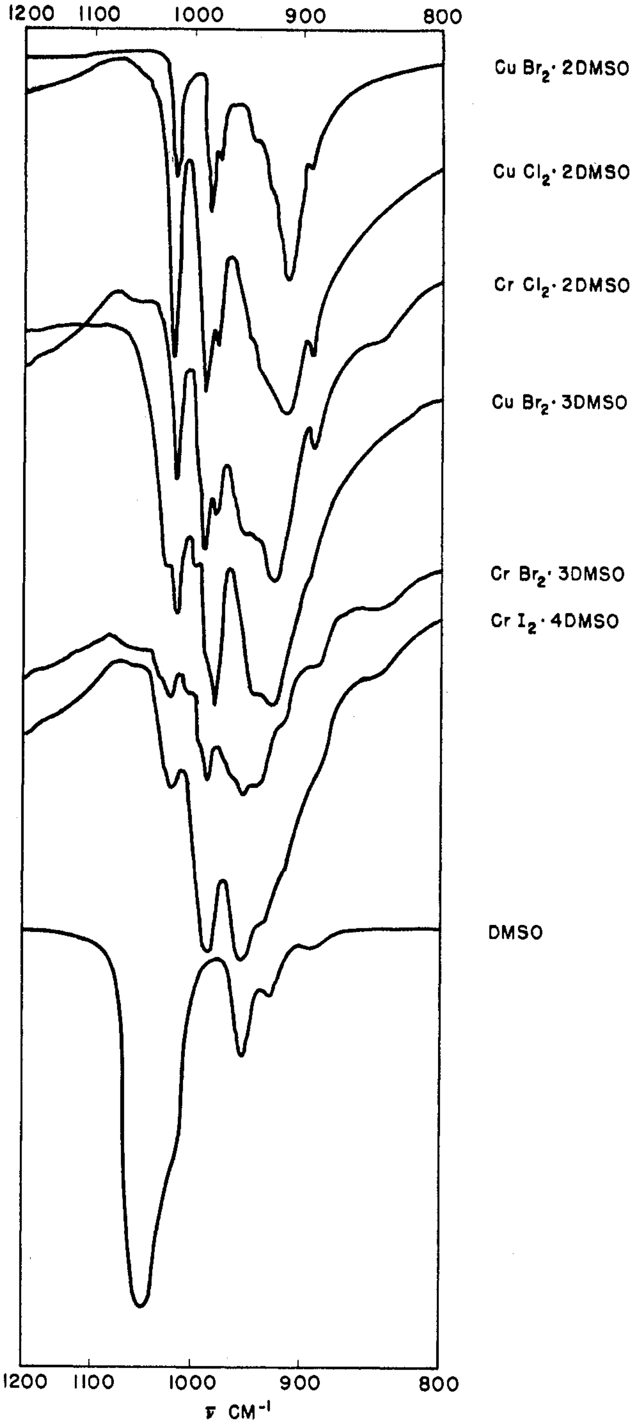

Figure 1.—Infrared spectra of the DMSO complexes in the 700–1200 cm.$^{-1}$ region in Nujol mulls.

spectra of $((CH_3)_4N)_2CuX_4$ are also included for comparison (see Figure 3).

TABLE II

SPECTRAL DATA (CM.$^{-1}$) (MOLAR EXTINCTION COEFFICIENTS IN PARENTHESES)

		$CrCl_2 \cdot 2DMSO$
Reflectance	*a*	12,000 vb, vs,[c] 17,000 w, sh, 18,200 w, 18,600 w, sh, 18,900 w
	b 8500(w,sh)	12,000 vb, vs, 17,450 w, 18,200 w, 18,600 w, 18,900 w
0.0230 *M* DMSO		12,000 (35.5) with excess[d] $Cl^- \rightarrow$ 10,600 (58)
0.226 *M* C_2H_5OH		12,500 (36.0) with excess $Cl^- \rightarrow$ 11,100 (43)
		$CrBr_2 \cdot 3DMSO$
Reflectance	*a*	12,200 vb, vs
	b	12,000–12,500 vb, vs
		$CrI_2 \cdot 4DMSO$
Reflectance	*a*	14,100
	b	15,400, 12,500 sh
		$CuCl_2 \cdot 2DMSO$
Reflectance	*a*	11,500 vb, vs
	b	11,400 vs, vb
0.0102 *M* DMSO		10,650 (~82)
0.0102 *M* CH_3NO_2		11,900 (~100) with excess $Cl^- \rightarrow$ 8300 (~105)
0.0115 *M* C_2H_5OH		11,000 (~70)
		$CuBr_2 \cdot 2DMSO$
Reflectance	*a*	~11,000 vs, vb
	b	11,100 vs, vb
0.1071 *M* CH_3NO_2		11,900 (~320) with excess $Br^- \rightarrow$ 8300 (~120)
0.00318 *M* C_2H_5OH		11,100 (~141)
0.0049 *M* DMSO		11,100 (~81.5)
		$((CH_3)_4N)_2CuCl_4$
Reflectance	*a*	~10,000–5000 vb, vs
	b	10,000, 6300
		$((CH_3)_4N)_2CuBr_4$
Reflectance	*a*	~10,000–5000 vb, vs
	b	9500, 6000

[a] Room temperature. [b] Liquid nitrogen temperature. [c] w, weak; sh, shoulder; v, very; s, strong. [d] Solid quaternary halide of a group V element added directly to the solution.

Some solution studies were carried out on $CrCl_2 \cdot 2DMSO$ and on the two copper(II) compounds in DMSO and ethanol. Spectra of the copper(II) compounds were also recorded in nitromethane, but this solvent appears to oxidize chromium(II). The slight differences between the solution spectra and the reflectance spectra are thought to be due to solvolysis, which appears to be more extensive with the copper(II) complexes than with $CrCl_2 \cdot 2DMSO$. Spectral changes are even more apparent when halide ions are added to the solutions. The pale green-yellow color of the $CuCl_2 \cdot 2DMSO$ solutions in ethanol, DMSO, and nitromethane changes immediately to the bright yellow color characteristic[14] of $CuCl_4^{2-}$ as the visible band moves into the near-infrared. Similarly, the straw-colored solution of $CuBr_2 \cdot 2DMSO$ in nitromethane changes to the deep violet color of $CuBr_4^{2-}$. Addition of large quantities of chloride ions to $CrCl_2 \cdot 2DMSO$ solutions also results in the band maximum moving to lower energies, although to a slightly lesser extent than in the copper(II) cases. Similar effects have been observed with the chromium(II)-acetonitrile complexes.[13]

Solution spectra of $CrBr_2 \cdot 3DMSO$ and $CrI_2 \cdot 4DMSO$ could not be obtained because of decomposition which occurred as they were redissolved. Even during their preparation it was necessary to crystallize them from ethanol as quickly as possible to avoid the formation of decomposition products.

---

(14) C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, **1**, 102 (1963).

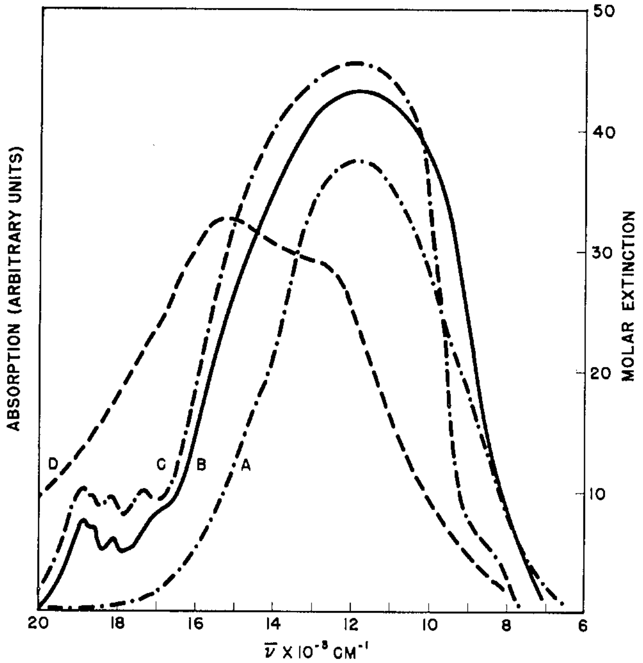

Figure 2.—Spectra of the Cr(II)–DMSO complexes between 4000 and 20,000 cm.$^{-1}$: A, $CrCl_2 \cdot 2DMSO$ solution in DMSO (0.0236 *M*); B, $CrCl_2 \cdot 2DMSO$ reflectance, at room temperature; C, $CrCl_2 \cdot 2DMSO$ reflectance, at 77°K.; D, $CrI_2 \cdot 4DMSO$ reflectance, at 77°K.

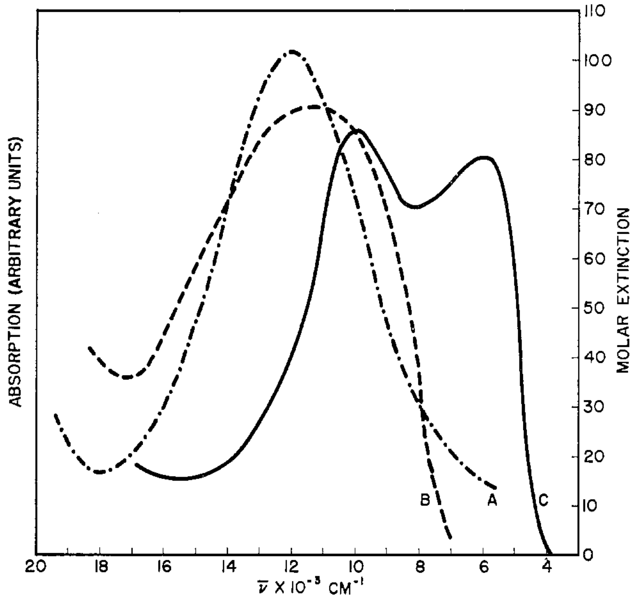

Figure 3.—Spectra of the Cu(II) complexes: A, $CuCl_2$ 2DMSO solution in nitromethane (0.011 *M*); B, $CuCl_2 \cdot 2DMSO$ reflectance, at 77°K.; C, $[(CH_3)_4N]_2[CuCl_4]$ reflectance, at 77°K.

X-Ray powder patterns of these complexes have been recorded and *d* spacings for the first ten lines (except for those which are too weak to measure accurately) are shown in Table III. $CrCl_2 \cdot 2DMSO$, $CuCl_2 \cdot 2DMSO$, and $CuBr_2 \cdot 2DMSO$ are isomorphous, although the *d* spacings in the bromide are, as expected, slightly greater. The pattern of $CuBr_2 \cdot 3DMSO$ was not obtained since the complex decomposed during grinding and packing in the tube. Although the patterns of $CuBr_2 \cdot 2DMSO$ and $CrBr_2 \cdot 3DMSO$ are similar, the complexes are not isomorphous. The complexes $MX_2 \cdot 2DMSO$ are not isomorphous with $MX_2 \cdot 2py$ (py = pyridine), although their X-ray patterns have some common features. $CrI_2 \cdot 4DMSO$ and $CrI_2 \cdot 4py$[1] also are not isomorphous.

Table III

d Spacings (Å.) Calculated from X-Ray Powder Patterns

$CrCl_2 \cdot$ 2DMSO	$CuCl_2 \cdot$ 2DMSO	$CuBr_2 \cdot$ 2DMSO	$CrBr_2 \cdot$ 3DMSO	$CrI_2 \cdot$ 4DMSO
8.31 s	8.21 s	8.51 s	8.55 m	7.89 m
a	*a*	7.34 w	7.30 m	6.17 s
6.51 vw	*a*	6.78 w	6.44 s	5.40 w
5.77 s	5.71 s	5.95 s	5.97 w	4.29 s
5.20 w	5.14 w	5.28 wv	5.67 s	3.90 m
4.69 s	4.65 w	4.83 m	4.77 s	3.44 s
4.41 w	4.47 s	4.46 m	4.29 s	3.21 m
4.00 m	4.05 s	4.16 m	4.12 w	3.13 w
3.78 m	3.82 s	3.90 m	3.97 m	3.03 s
3.68 m	3.66 m	3.71 s	3.83 m	2.95 s

[a] Very faint lines present. Visual intensities: s, strong; m, medium; w, weak; v, very.

Discussion

The strong absorption band found near 1100 cm.$^{-1}$ in DMSO vapor[15] and near 1050 cm.$^{-1}$, neat[8] (see Figure 1) or in CH_3NO_2 solution,[12] has been assigned[12,15] principally to the S–O stretching fundamental. Methyl group vibrations also appear near and are coupled with this fundamental.[15] In the oxygen-bonded complexes[4,5,8,12] the S–O stretch appears to move to lower frequencies. But since the shift is the result of two opposing effects,[5] a kinematic coupling which increases the frequency and a bond order decrease which lowers the frequency, the extent of the shift in any particular complex cannot be predicted.

For the complexes studied here, bonding through the sulfur atom can be eliminated.[5]

In spite of conflicting assignments[4,5,8,12] and the uncertainty in the amount of vibrational coupling, it appears reasonable to use the assignment of Cotton, *et al.*,[5] for the copper(II) halide complexes with DMSO. A similar assignment then is made for the chromium(II) halide–DMSO complexes. The small perturbations observed for the bands between 950 and 1020 cm.$^{-1}$ with changes in the metal or halide is to be contrasted with the obvious changes observed in the 900–950 cm.$^{-1}$ region. These changes suggest differences in the strength of DMSO coordination to the metal.

The complexity of the 950–1050 cm.$^{-1}$ region of the spectrum of the $MBr_2 \cdot 3DMSO$ complexes suggests that these DMSO molecules may exist in more than one type of chemical environment. The stability of the $CrBr_2 \cdot 3DMSO$ to loss of DMSO, unlike the $CuBr_2 \cdot 3DMSO$ complex, and the absence of a strong band near 1050 cm.$^{-1}$, suggest the DMSO groups are all coordinated to the metal. The visible spectrum (Table II) tends to reflect this also (albeit not covincingly), since the principal band at 12,200 cm.$^{-1}$ is shifted to slightly higher frequencies than the main absorbance in $CrCl_2 \cdot$

---

[15] W. D. Horrocks, Jr., and F. A. Cotton, *Spectrochim. Acta*, **17**, 134 (1961).

2DMSO in spite of the expected stronger crystalline field produced by the chloride in the latter complex. The general similarity of the infrared spectra of the $MBr_2 \cdot 3DMSO$ complexes suggests similar structures—perhaps halide-bridged distorted octahedral dimers.

The crystal structures[16–21] and electronic spectra[14,19–21] of $CuCl_4^{2-}$ and $CuBr_4^{2-}$ are well known. We have recorded (Table II) the reflectance spectra of $((CH_3)_4N)_2CuX_4$ (X = Cl, Br). The low-temperature spectrum of the chloride is shown in Figure 3. It is obvious from Figure 3 that there is no similarity between the spectra of $CuCl_4^{2-}$ and $CuCl_2 \cdot 2DMSO$, either in the solid state or in solution, at least for concentrations used in this study. Therefore the structures proposed by Meek, *et al.*,[4,12] *i.e.*, $[Cu(DMSO)_4][CuX_4]$, are ruled out.[22] Since $CuX_2 \cdot 2DMSO$ and $CrCl_2 \cdot 2DMSO$ are isomorphous, the chromium complex cannot be $[Cr(DMSO)_4][CrCl_4]$. While $CrCl_2 \cdot 2DMSO$ is not isomorphous with $CrCl_2 \cdot 2CH_3CN$,[13] or with $CrCl_2 \cdot 2py$,[1] the similarity of its X-ray powder pattern to that of the latter complex suggests the material probably also is polymeric in the solid state.[8] This presumably applies also to the copper(II) complexes.

The reflectance spectra of $CrCl_2 \cdot 2DMSO$ and $CrCl_2 \cdot 2py$ are quite different. Since DMSO is the weakest ligand,[7] excluding halide, yet studied with chromium(II) (*i.e.*, *Dq* is less than that for pyridine, acetonitrile, or water), the position of the high-energy band seen in complexes with pyridine,[7] acetonitrile,[13] and water,[11] and which is thought[11] to contain the transition corresponding to 10*Dq*, will be reduced in energy in the DMSO complexes. It has already been noticed in other complexes[1,11,13] that the band in the 10,000 cm.$^{-1}$ region is less influenced by different ligands than the main absorption, so in these DMSO complexes it seems that the high-energy band has coalesced with the lower energy band to give one very broad band. Thus it appears that the levels arising from $^5T_{2g}$ (in O_h) and the upper component[11] of ^5E_g (in O_h) in these complexes occur at nearly the same energy.

The shoulder at ~8500 cm.$^{-1}$ in the reflectance spectrum of $CrCl_2 \cdot 2DMSO$ at low temperatures appears too weak to be the transition to the levels of the split ^5E_g ground state and may be the spin-forbidden transition[11] to $^3T_{1g}$ (in O_h). The weak bands between 17,000 and 20,000 cm.$^{-1}$ are spin-forbidden transitions to other higher energy trplet states,[23] as were observed[11] in $CrCl_2$.

The spectrum of $CrI_2 \cdot 4DMSO$ at low temperatures shows (Figure 2) a distinct shoulder. However, the center of the band system is at surprisingly high energies, and, in fact, the shoulder appears in the same position as the low-energy component in the spectrum[1] of $CrI_2 \cdot 4py$. The two compounds may have quite similar structures; that is, four ligands in a plane bonded to the chromium and two *trans* (or *cis*) halides. The fact that $CrI_2 \cdot 4DMSO$ absorbs at considerably higher energies than $CrCl_2 \cdot 2DMSO$ suggests that the six-coordination of the chromium is made up of two iodides and four DMSO molecules in the former complex and four chlorides and two DMSO molecules in the latter complex.

While the spectra of the copper(II) compounds in solutions show some evidence for solvolysis and the complexes readily form tetrahedral CuX_4^{2-} when halide ions are added, $CrCl_2 \cdot 2DMSO$ appears much more reluctant to form a tetrahedral species. As noted earlier, the $MX_2 \cdot 2DMSO$ species are probably polymeric. The spectral data support this conclusion.

Acknowledgments.—The support of the National Science Foundation, GP-196, is gratefully acknowledged.

---

[16] L. Helmholz and R. F. Kruh, *J. Am. Chem. Soc.*, **74**, 1176 (1952).

[17] B. Morosin and E. C. Lingafelter, *Acta Cryst.*, **13**, 807 (1960).

[18] B. Morosin and E. C. Lingafelter, *J. Phys. Chem.*, **65**, 50 (1961).

[19] B. Morosin and K. Lawson, *J. Mol. Spectry.*, **12**, 98 (1964); **14**, 397 (1964).

[20] A. G. Karipides and T. S. Piper, *Inorg. Chem.*, **1**, 970 (1962).

[21] J. Ferguson, *J. Chem. Phys.*, **40**, 3406 (1964).

[22] While some ionization of $CuX_2 \cdot 2DMSO$ in CH_3NO_2 to Cu^{2+}(solvated),X^- cannot be excluded, certainly little CuX_4^{2-} could be formed without detection. Addition of halide ions, however, does cause the formation of this species.

[23] Reference to the $3d^4$ energy level diagram recently completed by A. D Liehr shows the enormous number of triplet and singlet states between 15,000 and 35,000 cm.$^{-1}$. Indeed, the diagram is so complex in this region that assignment of the observed spin-forbidden bands appears hopeless at present. The authors wish to thank Dr. Liehr for copies of his diagrams prior to publication.