

Polarized Crystal Spectra of the Mixed Metal Salt $[(\text{CH}_3)_3\text{NH}]\text{Mn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$

MARTHA J. LINDBECK,* JOHN E. DRUMHELLER,†
 AND KENNETH EMERSON*

*Department of Chemistry, †Department of Physics, and Montana State
 University, Bozeman, Montana 59717

Received June 13, 1983; in revised form December 9, 1983

The electronic absorption spectra in two polarizations are reported for crystals of the dichroic salt, $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ where TMA represents the trimethylammonium cation, $(\text{CH}_3)_3\text{NH}^+$. Although $\text{TMA CuCl}_3 \cdot 2\text{H}_2\text{O}$ is monoclinic, the mixed metal salts in which $x \geq 0.20$ adopt the orthorhombic structure of $\text{TMAMnCl}_3 \cdot 2\text{H}_2\text{O}$. The bands observed in the near ir region are adequately explained as $d-d$ transitions of the Cu(II) ion in D_{2h} symmetry. Other polarized bands which occur in the visible region and are neither Mn(II) nor Cu(II) $d-d$ transitions are discussed.

Introduction

A great deal of spectroscopic data on the Cu(II) ion exists in the chemical literature, but very few workers have attempted to assign energy levels for this ion in orthorhombic symmetry. Smith (1) has reviewed chlorocuprate(II) complexes in various environments. Two salts containing planar CuCl_4^{2-} units have been studied in D_{2h} symmetry. The polarized crystal spectra of (methylphenethylammonium) $_2\text{CuCl}_4$, hereafter referred to as $\text{MPA}_2\text{CuCl}_4$, have been reported by Hitchman and Cassidy (2). Hitchman (3) also investigated a similar compound, (creatininium) $_2\text{CuCl}_4$, abbreviated $\text{CRE}_2\text{CuCl}_4$. In the present work crystal spectra in two polarizations are reported for light incident upon the (100) face of the orthorhombic mixed metal salt $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ which contains

chains of edge-shared $\text{MCl}_4(\text{H}_2\text{O})_2$ octahedra. The spectrum of the TMA salt in one polarization is virtually identical to one obtained by Hitchman for $\text{CRE}_2\text{CuCl}_4$.

This mixed metal salt is also dichroic, exhibiting amber and green crystal faces. Two polarized bands occur in the visible region of the spectra which are not seen in the spectra of either of the pure end members. Based on the energy level diagram proposed for D_{2h} symmetry, they cannot be described as $d-d$ transitions of either divalent ion. Schmid *et al.* (4) have reported that small amounts of Cu(II) doped into $\text{enH}_2\text{MnCl}_4$ where $\text{enH}_2 = \text{NH}_3\text{C}_2\text{H}_4\text{NH}_3$ result in deep-red crystals. In this paper we address the possibility that the bands giving rise to the colors of these two mixed metal salts may have the same origin.

Crystal Structures

The crystal structure of TMAMn

* To whom correspondence should be addressed.

$\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ has been reported by Caputo *et al.* (5); this orthorhombic salt crystallizes in the $Pnma$ space group. The Cu analog, $\text{TMA CuCl}_3 \cdot 2\text{H}_2\text{O}$, is monoclinic, crystallizing in the $P2_1/c$ space group as reported by Losee *et al.* (6). Mixed metal salts, $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ with $x \geq 0.20$ crystallize in the orthorhombic space group, $Pnma$; when $x < 0.20$ the crystals adopt the monoclinic structure, space group $P2_1/c$. Figure 1 illustrates the relationship between the polarization directions and unit cell axes within the $\text{MCl}_4(\text{H}_2\text{O})_2$ chains for these two structures. In terms of the chromophore the (001) face of the monoclinic crystal is identical to the (100) face of the orthorhombic crystal.

Experimental Section

Sample Preparation

Single crystals of $\text{TMAMnCl}_3 \cdot 2\text{H}_2\text{O}$, $\text{TMA CuCl}_3 \cdot \text{H}_2\text{O}$, and $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ were grown by slow evaporation of aqueous solutions containing stoichiometric amounts of trimethylamine hydrochloride and the divalent metal chlorides. The orthorhombic mixed metal crys-

tals with high Mn content tended to grow as hexagonal plates elongated along [010] with well-developed (100) faces where () denoted a plane and [] denote the normal to a plane. The monoclinic crystals of the pure Cu analog can be grown as laths with the needle axis parallel to [100] and with well-developed (001) faces. A quite different habit is observed in the structural transition region for the mixed metal crystals which retain the orthorhombic structure. These crystals are flattened octahedra slightly elongated along [100] of the $Pnma$ unit cell.

The (100) faces of the mixed metal crystals with high Mn content appear amber in polarized light with the electric vector parallel to [010] and green in polarized light with the electric vector parallel to [001]. As the Cu content increases, the amber color disappears; in crystals in which the Cu content is high enough to produce the monoclinic structure green is the only color observed.

The orthorhombic crystals exhibit parallel extinction on all faces. Monoclinic crystals of $\text{TMA CuCl}_3 \cdot 2\text{H}_2\text{O}$ exhibit parallel extinction for the (001) face, but an extinction angle of approximately 30° from the a axis is observed for the (010) face. These extinction directions within the unit cell of $\text{TMA CuCl}_3 \cdot 2\text{H}_2\text{O}$ are identical to those reported by Ferguson and Wood (7) for $\text{CoCl}_2 \cdot 2\text{H}_2\text{O}$ which possesses the same chromophore geometry.

Absorption Spectroscopy

Spectra of single crystals of $\text{TMAMnCl}_3 \cdot 2\text{H}_2\text{O}$ were collected for all three possible polarizations in the orthorhombic cell. Spectra of the monoclinic salt, $\text{TMA CuCl}_3 \cdot 2\text{H}_2\text{O}$, were recorded with polarized light incident on the (001) face only. Spectra of the mixed metal analog, $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$, in the orthorhombic structure were obtained from the (100) face. All spectra were recorded on a Cary 14 spectrophotometer; orientation of the crystal

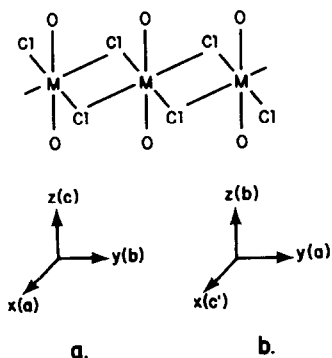


FIG. 1. Location of unit cell axes and polarization directions with respect to the chromophore in (a) the orthorhombic salt $\text{TMAMnCl}_3 \cdot 2\text{H}_2\text{O}$ and (b) the monoclinic salt $\text{TMA CuCl}_3 \cdot 2\text{H}_2\text{O}$.

faces was checked using precession photographs.

When referring to the polarization directions in the following discussion, the notation \hat{x} - L is used to designate light in which the electric vector is parallel to the x coordinate or a crystallographic axis, similarly for y - and z -polarized light. The D_{2h} symmetry operators for \hat{x} - L , \hat{y} - L , and \hat{z} - L are B_{3u} , B_{2u} , and B_{1u} , respectively.

Results

Manganese(II) Spectra

For complexes containing high spin Mn(II) all $d-d$ transitions are spin forbidden. The polarized crystal spectra of $\text{TMAMnCl}_3 \cdot 2\text{H}_2\text{O}$ in D_{2h} symmetry has been discussed in another paper (8). No bands are observed for this ion in the near ir region, and bands in the visible region are easily distinguished from those due to the Cu(II) ion because of their very weak intensity.

Copper(II) Spectra

Polarized crystal spectra were recorded for the (001) face of $\text{TMACuCl}_3 \cdot 2\text{H}_2\text{O}$; Fig. 1 illustrates the chromophore orientation of this face. Although very thin crystals were used to collect the Cu(II) spectra, the intensity of the transitions due to the d^9 ion drove the bands off scale. Another problem encountered with the crystals of the pure Cu analog is their extreme sensitivity to heat and light. When exposed to the ir source of the Cary 14, which is located in the compartment adjacent to the sample cell, these crystals decompose very quickly. Thus, very little spectroscopic data could be obtained from the ir spectra of $\text{TMACuCl}_3 \cdot 2\text{H}_2\text{O}$. No bands were recorded in the visible region for this salt.

Manganese(II)-Copper(II) Spectra

Because there are no bands in the near ir due to Mn(II) any bands in this region of the

spectra of $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ should be due to Cu(II). The spectra shown in Figs. 2 and 3 were recorded from the (100) face of the Mn-Cu mixed metal crystals. In \hat{y} - L these crystals are amber; in \hat{z} - L they are green. Four bands can be identified in the near ir for the Cu(II) spectra obtained, but even though crystals with the lowest mole fraction of Cu available were used, only one band remains on scale. Due to the habit of the Mn-Cu crystals only the \hat{y} - L and \hat{z} - L spectra were accessible. A large band, the top of which is off scale, appears in the near ir in \hat{y} - L ; interpolation indicates that the top of this band lies at 805 nm. In \hat{z} - L a broader double band appears; the tops of both are off scale, but interpolation suggests band maxima at 860 and 895 nm. In both of these polarized spectra a well-defined shoulder is evident at 960 nm.

In the visible portion of the Mn-Cu spectra presented in Fig. 3 a band appears at 548 nm in \hat{y} - L which is not present in \hat{z} - L . It is not observed in the spectra of either of the

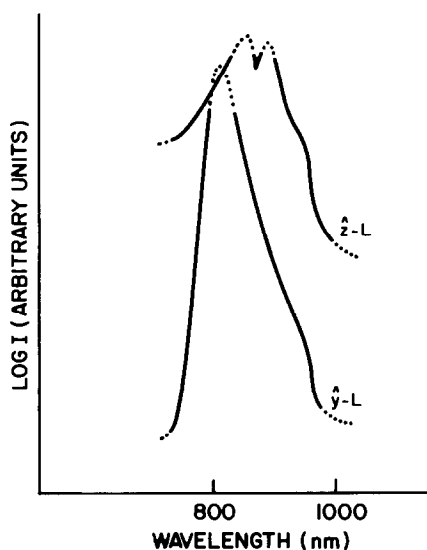


FIG. 2. Polarized crystal spectra of $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ in the near ir region. Light in which the electric vector is parallel to x is designated \hat{x} - L , similarly for \hat{y} - L and \hat{z} - L .

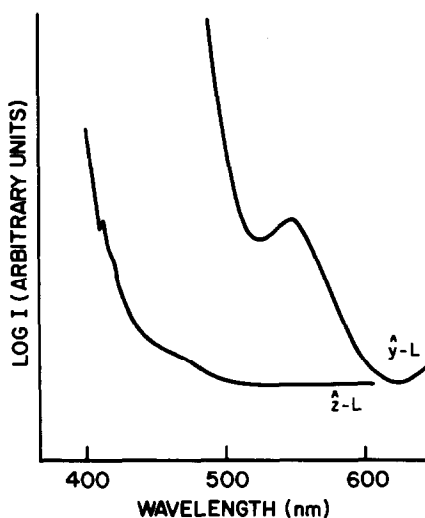


FIG. 3. Polarized crystal spectra of $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ in the visible region.

pure salts. The tail of a large band in the uv region extends to 400 nm in \hat{z} -L while in \hat{y} -L the visible spectrum goes off scale at 480 nm. Although the top of this band is not seen in \hat{y} -L, it can be inferred from the spectrum in \hat{z} -L. Because the band in the pure Mn(II) spectra which occurs at 460 nm is too weak to be observed in the mixed salt and is also forbidden in \hat{z} -L, the shoulder at 465 nm in \hat{z} -L must be an artifact of the absorption band observed in \hat{y} -L. If this is indeed the case, its location suggests that it may be the source of the amber color observed in \hat{y} -L.

Discussion

Although the peaks are not located at the same wavelengths, the spectrum of $\text{CRE}_2\text{CuCl}_4$ in \hat{z} -L recorded by Hitchman (3) has the same shape as the spectrum of $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ in \hat{y} -L. The chromophore in both $\text{CRE}_2\text{CuCl}_4$ and $\text{MPA}_2\text{CuCl}_4$ is the planar CuCl_4^{2-} unit with distortion of the Cu-Cl bonds producing D_{2h} symmetry for the metal site. The Cu-Cl bond lengths in $\text{CRE}_2\text{CuCl}_4$ are 2.23 and

2.27 Å (9). In the chromophore of the TMA salt, $\text{CuCl}_4(\text{H}_2\text{O})_2$, the Cu-O bond length is about 2.0 Å and the two Cu-Cl bond lengths are 2.3 and 2.8 Å (6). These differences in geometry are sufficient to account for the differences in peak location. Another factor to be considered in the mixed metal salt is that the Cu(II) ion has been doped into an orthorhombic site dominated by the Mn(II) ion. In $\text{TMAMnCl}_3 \cdot 2\text{H}_2\text{O}$ the Mn-O bond distance is 2.2 Å and the Mn-Cl bond distances are 2.5 and 2.6 Å (5). This suggests that the d^9 ion is forced into an octahedral site in which the axial dimensions are shorter than normal for Cu(II), although the actual environment is probably somewhere between those found in the two pure end members. Table I provides a comparison of cell parameters in crystals of $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ as x varies.

As indicated in Fig. 1 the coordinate axis system has been defined so that x , y , and z correspond to the a , b , and c crystallographic axes in the orthorhombic unit cell. In $\text{CRE}_2\text{CuCl}_4$ which crystallizes in the monoclinic space group, $P2_1/c$, Hitchman's z axis lies along the c crystallographic axis and is perpendicular to the CuCl_4 plane. This also represents the long axis for the Cu(II) ion in the CuCl_4 chromophore. A conventional choice of axes in the TMA salt would place z along the longer of the two Cu-Cl bonds. However, light polarized parallel to the two bonding directions within the MCl_4 plane of the orthorhombic TMA salts yields

TABLE I
CELL DIMENSIONS IN CRYSTALS OF
 $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ AS x VARIES

x	a (Å)	b (Å)	c (Å)
1.00	16.58	7.434	8.227
0.80	16.64	7.469	8.095
0.00 ^a	16.73	7.479	7.864

^a See text for comparison of axes in Cu salt.

identical spectra. Because different spectra are observed only if light polarized parallel to the unit cell directions is used, these axes have been chosen as coordinate axes.

There are only five possible electron configurations for the d^9 ion, and the symmetry of the state is that of the orbital occupied by the unpaired electron. A Tanabe-Sugano diagram (10) for the Cu(II) ion indicates that the 2D Russell-Saunders term splits into $T_{2g} + E_g$, the latter being the ground state, in octahedral symmetry. In D_{2h} symmetry E_g splits into $A_g + A_g$ and T_{2g} splits into $B_{1g} + B_{2g} + B_{3g}$. Based on the spectral data the band at 960 nm is assigned as the unpolarized $A_g \rightarrow A_g$ transition. The band at 860 nm which is visible in \hat{z} - L and vanishes in \hat{y} - L is the $A_g \rightarrow B_{2g}$ transition. The highest energy ir band occurs at 805 nm and represents the $A_g \rightarrow B_{1g}$ transition forbidden in \hat{z} - L . This produces the energy level diagram shown in Table II.

The $d-d$ transitions of both Cu(II) and Mn(II) are well documented in the literature and can be assigned in the TMA salts as indicated above. Preparation of the mixed metal salt $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ where $x > 0.25$ results in amber/green crystals which display additional polarized bands in the visible region. These bands, located at 465 and 548 nm, are not seen in either pure end member. There are a number of ways in which these bands can be explained; possibilities include a $\text{Cl} \rightarrow \text{Cu}$

charge transfer involving a Cu(II) ion in an unusual environment, the presence of $\text{Cu}_2\text{Cl}_6^{2-}$ dimers or the existence of Mn(III) ions.

Schmid *et al.* (4) have reported a band at 480 nm which is responsible for the red color observed in $\text{enH}_2\text{MnCl}_4$ doped with small amounts of Cu(II). Because the chromophore for this salt, MCl_6 , is similar to that in the TMA salt, $\text{MCl}_4(\text{H}_2\text{O})_2$, this band at 480 nm may have the same origin as the band at 465 nm in the TMA salt. Schmid *et al.* (4) suggest that the source of the band in their salt is a $\text{Cl} \rightarrow \text{Cu}$ charge transfer which occurs at a very low energy because the Cu(II) ion exists in a strained environment in the Mn(II) host lattice. Comparison of the bond distances in $\text{TMAMnCl}_3 \cdot 2\text{H}_2\text{O}$ and $\text{TMACuCl}_3 \cdot 2\text{H}_2\text{O}$ along with the cell parameter data presented in Table I indicate that the Cu(II) ion in $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ is also forced into an unusual geometry. In crystals of both these mixed metal systems the Cu(II) ion must occupy a lattice site dominated by Mn(II) which will distort the usual Cu(II) geometry.

Additional support for assigning a common origin to these two bands in the mixed metal systems lies in the observed colors. If the band at 480 nm is the source of the red color in the doped enH_2 salt, a similar band at a lower wavelength ought to produce the amber color observed in the TMA salt. Thus, these two bands can reasonably be assigned the same origin, that being an unusually low energy $\text{Cl} \rightarrow \text{Cu}$ charge transfer involving a strained Cu(II) ion.

Because of its low energy, it is unlikely that the polarized band at 548 nm is a charge transfer band even if a strained Cu(II) ion is involved. This band may be due to the presence of $\text{Cu}_2\text{Cl}_6^{2-}$ dimers within the lattice. Willett and Liles (11) have observed a polarized band at about 530 nm in several red Cu(II) salts which they interpret as a transition involving the $\text{Cu}_2\text{Cl}_6^{2-}$ dimer. The band in the TMA salt is

TABLE II
PROPOSED ENERGY LEVEL DIAGRAM FOR Cu(II) IN
 D_{2h} SYMMETRY

Representation in D_{2h}	Observed peaks	Forbidden polarization predicted	Forbidden polarization observed
B_{1g}	805	z	z
B_{2g}	860	y	y
B_{3g}	895	x	$y?$
A_g	960	None	None
A_g			

located at about the same wavelength and has the same polarization. However, given the low concentration of Cu(II) within the lattice and assuming random distribution, it seems unlikely that such dimers would form in $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$.

Another possible explanation of the band at 548 nm involves the existence of Mn(III). Schmid *et al.* (4) considered a $\text{Mn} \rightarrow \text{Cu}$ electron transfer as the origin of the band at 480 nm in $\text{enH}_2\text{MnCl}_4$ doped with Cu(II), but rejected this explanation because this band was not observed in $\text{enH}_2\text{CuCl}_4$ doped with Mn(II). However, if such a transfer does occur, two new metal ions are formed. Although no new peaks are expected for Cu(I), a d^{10} ion, $d-d$ transitions in Mn(III), a d^4 ion, may be a viable source of the peak in the mixed metal systems. Possible splitting arrangements for Mn(III) in D_{4h} and D_{2h} symmetries are presented in Table III. The observed polarization data may be explained as a transition to B_{2g} in D_{4h} or to B_{1g} in D_{2h} . Both of these transitions are forbidden in $\hat{\sigma}$ -L. If other transitions occur for Mn(III), they are lost beneath the larger bands due to Cu(II) in the near ir and uv regions.

Spectra of Mn(III) in several environments appear in the literature. Solution spectra of Mn(III) in 10 N HCl yield a peak between 550 and 575 nm (12). Piper and Carlin (13) observed a peak at 498 nm in the polarized crystal spectra of Mn(III) doped

into $\text{NaMgAl}(\text{C}_2\text{O}_4)_3 \cdot 9\text{H}_2\text{O}$. Hatfield *et al.* (14) report a peak at 570 nm in the powdered reflectance spectrum of a salt containing MnCl_6^{3-} as a chromophore. Polarized spectra of $\text{Mn}(\text{H}_2\text{O})_6^{3+}$ yields a peak at 476 nm (15). If a linear correlation exists for spectra of $\text{MnCl}_x(\text{H}_2\text{O})_y$, based on literature data one would expect $\text{MnCl}_4(\text{H}_2\text{O})_2$ to absorb at 539 nm which is very close to the observed value of 548 nm in the TMA salt.

The extent of the $\text{Mn} \rightarrow \text{Cu}$ electron transfer within the crystal lattice must also be considered. If oxidation is complete, in $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ when x is very small no Mn(II) peaks should appear and when x is very large no Cu(II) peaks should appear. However, if only a fraction of the metal sites participate in the electron transfer, $d-d$ transitions for all three ions may be observed. In this case crystals with very little Mn(II) may not generate sufficient Mn(III) to produce a peak. This would account both for the presence of Mn(II), Mn(III), and Cu(II) $d-d$ transitions in $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ for $0.8 > x > 0.5$ and for the gradually increasing dominance of the green color as x decreases until at $x < 0.25$ the mixed crystals resemble the pure Cu salt. Based on the evidence presented above, a strong argument can be made for assigning the polarized peak at 548 nm in the mixed metal TMA salt as a Mn(III) $d-d$ transition. It would appear that $\text{enH}_2\text{Mn}_{0.9986}\text{Cu}_{0.0014}\text{Cl}_4$ contains too little Mn(III) to produce a peak.

TABLE III
POSSIBLE SPLITTING
ARRANGEMENTS FOR Mn(III) IN
 D_{4h} AND D_{2h} SYMMETRIES

O_h	D_{4h}	D_{2h}
	$-E_g$	$-B_{3g}$
T_{2g}	$-B_{2g}$	$-B_{2g}$
	$-B_{1g}$	$-B_{1g}$
E_g	$-B_{1g}$	$-A_g$
	$-A_{1g}$	$-A_g$

Conclusion

The electronic absorption spectra in two polarizations are reported for crystals of $\text{TMAMn}_x\text{Cu}_{1-x}\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ where TMA represents $(\text{CH}_3)_3\text{NH}^+$. The bands observed in the near ir region are adequately explained as $d-d$ transitions of the Cu(II) ion in D_{2h} symmetry. One polarized band in the visible region is assigned as a Mn(III) $d-d$ transition where the Mn(III) ion is generated

via a Mn \rightarrow Cu electron transfer. Another higher energy band is assigned a Cl \rightarrow Cu charge transfer where the Cu(II) exists in a strained environment because it is forced to occupy sites in a Mn(II) lattice.

References

1. D. W. SMITH, *Coord. Chem. Rev.* **21**, 93 (1976).
2. M. A. HITCHMAN AND P. CASSIDY, *Inorg. Chem.* **18**, 745 (1979).
3. M. A. HITCHMAN, *J. Chem. Soc., Chem. Commun.* 973 (1979).
4. U. SCHMID, H. GUDEL, AND R. WILLETT, *Inorg. Chem.* **21**, 2977 (1982).
5. R. E. CAPUTO, R. D. WILLETT, AND J. A. MUIR, *Acta Crystallogr. Sect. B* **32**, 2639 (1976).
6. D. B. LOSEE, J. N. MCEARNEY, G. E. SHANKLE, R. L. CARLIN, P. J. CRESWELL, AND W. T. ROBINSON, *Phys. Rev. B.* 4342 (1972).
7. J. FERGUSON AND T. E. WOOD, *Inorg. Chem.* **14**, 190 (1975).
8. M. J. LINDBECK, J. E. DRUMHELLER, AND K. EMERSON, in press.
9. M. R. UDOPA AND B. KREBS, *Inorg. Chim. Acta* **33**, 241 (1979).
10. Y. TANABE AND S. SUGANO, *J. Phys. Soc. (Jpn.)* **9**, 753 (1954).
11. R. D. WILLETT AND O. L. LILES, JR., *Inorg. Chem.* **6**, 1666 (1976).
12. J. P. FACKLER, JR., AND I. D. CHAWLA, *Inorg. Chem.* **3**, 1130 (1964).
13. T. S. PIPER AND R. L. CARLIN, *J. Chem. Phys.* **35**, 1809 (1961).
14. W. E. HATFIELD, R. C. FAY, C. E. PFLUGER, AND T. S. PIPER, *J. Amer. Chem. Soc.* **85**, 265 (1963).
15. O. G. HOLMES AND D. S. MCCLURE, *J. Chem. Phys.* **26**, 1686 (1957).