Inorganica Chimica Acta, *84* (1984) 7–12

Spectroscopic Investigation of the Tetrachlorocobaltate(II), -nickelate(II) and -cuprate(II) Salts of 2-,3- and 4-Acetylpyridinium Cations

DOUGLAS X. WEST*, TIMOTHY J. PARSONS, and ROGER K. BUNTING

Department of Chemistry, Illinois State University, Normal, Ill. 61761, U.S.A.

Received August 4, 1983

Tetrachlorocobaltate(II) salts of 2-acetyl-, 3-acetyl- and 4-acetylpyridinium ions as well as tetrachloronickelate(II) and -cuprate(II) salts of 3-acetylpyridinium ion have been prepared and characterized primarily by spectral methods. The latter two transition metal chlorides gave chlorometallate(II) salts with the 4-acetylpyridinium ion, but only 2-acetylpyridine complexes of these two ions could be isolated. The infrared spectra suggest polymeric species for both of the nickelate salts as well as $[4\text{-}AcetPyH]_n[CuCl_3]_n$ *based on the low energy of their* ν_{M-Cl} *bands and the thermochromic nature of* $[3\text{-}AcetPyH]_2[NiCl_4]$. *The spectral and thermal properties of the three cobaltate salts indicate that they are very similar and that their distortion from tetrahedral symmetry is small. The ESR and electronic spectra of* $[3\text{-}AcetPyH]_2[CuCl_4]$ *confirm it to have* D_{2d} *symmetry while suggesting that* $[4\text{-}AcetPyH]_n[CuCl_3]_n$ *does not involve the well characterized* $Cu_2Cl_6^{2-}$.

Introduction

The various chlorocuprate(II) salts have been extensively investigated because of the large number of stereochemistries they assume [1]. While most of the studies of the tetrachlorocuprate(II) ion have featured alkylammonium counterions, there have been only a few reports concerning halocuprates(II) prepared with substituted pyridinium ions. One group has prepared tetrachlorocuprates(II) of the amino-substituted pyridinium ions [2] as well as other pyridinium ions [3], but limited their studies to the infrared characterization of the cations. One of us has recently been involved in a more extensive spectroscopic study of some aminopyridinium tetrachlorocuprate(II) salts [4]. In addition, the literature is sparce on reports of the analogous cobaltate(II) and nickelate(II) salts. The quinolinium salts have been characterized [5], but substituted pyridinium salts have, to our knowledge, not been studied. Of interest is the thermochromic character of the alkyl- and arylammonium tetrachloronickelates [6] and whether this same behavior will occur with these solids. Another reason for preparing and characterizing new solids of this nature is the recent report of two modifications [7] of the N-(2-ammonioethyl)-morpholinium tetrachlorocuprate(II). Other examples should be possible. In this communication we report on the properties of seven new solids featuring chlorometallate anions and the 2-acetyl-, 3-acetyl- and 4-acetylpyridinium cations.

Experimental

The acetylpyridinium chloride salts were isolated by bubbling gaseous HCl into acetone–ether solutions of the acetylpyridines. Preparation of the chlorometallate solids was accomplished in two different ways: the first method was essentially the same as reported previously [4] (*i.e.* refluxing in equal volume HCl–EtOH mixtures). The second involved mixing alcoholic solutions of 2-acetylpyridinium hydrochloride and the anhydrous metal chloride in a 2:1 molar ratio and then treating solutions as in the first method. A third attempt involved bubbling HCl into a mixture of the appropriate pyridine and the metal chloride in a variety of solvents, but this resulted only in the formation of acetylpyridine complexes.

Partial elemetal analyses were performed by Micro Analysis of Wilmington, Delaware. The spectroscopic measurements were performed using procedures and instrumentation identical to those of previous reports from this laboratory [8]. The thermal studies were carried out on Perkin-Elmer TGS-2 and DSC-2C Systems.

Results and Discussion

The colors, thermal properties and partial elemental analyses for the unique solids isolated from the various preparative attempts are shown in Table I.

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*Author to whom all correspondence should be addressed.

0020-1693/84/$3.00

TABLE I. Analytical Data.

Compounds	Color	Thermal Changes (°C)[a]		Analyses		
				C	H	N
$[2AcetPyH]_2[CoCl_4]$	Royal blue	142(8.9)	Calcd:	37.78	3.62	
			Found:	37.59	3.75	
$[3AcetPyH]_2[CoCl_4]$	blue	91(7.2)	Calcd:	37.78	3.62	
			Found:	37.80	3.69	
$[4AcetPyH]_2[CoCl_4]$	Royal blue	137(7.6)	Calcd:	37.78	3.62	6.29
			Found:	37.78	3.67	6.67
$[3AcetPyH]_2[NiCl_4]\cdot 3H_2O$	dull green	85(21.8)	Calcd:	33.70	4.45	5.62
		114(3.6)	Found:	33.69	4.35	6.22
$[4AcetPyH]_3[NiCl_5]$	yellow	nothing	Calcd:	41.87	4.02	6.98
		to 327 °C	Found:	42.55	4.01	6.86
$[3AcetPyH]_2[CuCl_4]$	bright	142(8.7)	Calcd:[b]	37.40	3.59	6.23
	yellow-green	222(14.7)	Found:	37.91	3.61	5.75
$[4AcetPyH]_n[CuCl_3]_n nH_2O$	yellow-green	105(13.6)				
		117(2.8)	Calcd:	27.12	3.24	
		149(5.2)	Found:	27.19	3.22	
		170(9.6)				

[a] All changes endothermic and numbers in parentheses are enthalpy changes in kcal mol^{-1}. [b] %Cl: Calcd: 31.54; Found: 31.33.

We have been unable to prepare the 2-acetylpyridinium salts of either a chloronickelate(II) or chlorocuprate(II) ion and have, instead, isolated complexes involving the bidentate 2-acetylpyridine ligand. Some of these complexes, evidently because of the extreme conditions (refluxing HCl–EtOH) used in their preparation, are unique to those that have previously been reported [9] and will be the subject of a later communication. The blue colors of the chlorocobaltate(II) salts are indicative of an approximately tetrahedral stereochemistry, while the green or yellows of the nickelate and cuprate salts are less diagnostic of stereochemistry. However, their various shades suggest differences in the anions. This is confirmed by the results of the partial elemental analyses which show that the 3-acetyl salts are tetrachlorometallates, but the 4-acetyl salts of these two metal ions are not.

While there is a significant difference between the decomposition temperatures of the three cobaltate salts (Table I), their enthalpies of decomposition are similar. The similarity is suggestive of nearly identical hydrogen bonding and of little effect being brought about by the position of the acetyl group for this series of salts. The melting points of the 2-, 3- and 4-acetylpyridinium chlorides are the following: 190°, 180° and 136 °C, the latter solid having the same value as that of the analogous $CoCl_4^{2-}$ salt.

As has been found for the alkylammonium tetrachloronickelates [6], the 3-acetyl salt, after losing the hydrate water molecules, changes from green to blue green and finally to a royal blue at approximately 115 °C. The higher temperature form is known to be the blue tetrahedral $NiCl_4^{2-}$, and its formation occurs at a transition temperature similar to those reported earlier, in fact, at the identical temperature of the benzylmethylammonium salt. However, the colors of the two low temperature forms are somewhat different, the ammonium salts being described as brown-yellow [6]. These ammonium salts were shown to be octahedral polymeric materials containing bridging chlorines. Inspection of Table II shows that the bands assigned to the ν_{Ni-Cl} stretching modes of the 3-acetylpyridinium salt are in agreement with this interpretation. Their lower energies indicate a higher coordination number than that of the cobalt salts, and the band at 230 cm^{-1} is assignable to the stretching frequency of a bridging chloride. In contrast, the 4-acetyl pyridinium salt isolated with the chloronickelate ion analyzes as a pentachloronickelate. It does not change color up to greater than 300 °C and shows no DSC peaks up to that temperature. Its ν_{Ni-Cl} bands are similar, however, and a polymeric structure is envisioned for it as well. It will be further considered later in this report.

As opposed to the tetrachlorocuprates formed with aminopyridinium ions which were various shades of yellow, the 3-acetylpyridinium salt is a bright yellow-green. Its temperature of the first transition and its enthalpy change are similar to those found for the tetrachlorocobaltates. However, there is a second transition in this copper salt which is not present in

TABLE II. Partial Infrared Assignments (cm^{-1}) of the 2-, 3- and 4-Acetylpyridinium Chlorides and Their Chlorometallate Salts.

Compound	Band Assignment				
	ν_{OH}	ν_{Py-H}	$\nu_{C=O}$	$\nu_{C=N^+}$	ν_{M-Cl}
2-AcetPyH$^+$Cl$^-$		2325s 2075m	1707s	1607s	
[2-AcetPyH]$_2$[CoCl$_4$]		2318s	1707vs	1601s	302vs 295sh 282sh
3-AcetPyH$^+$Cl$^-$		2420s, b 2118m	1693vs	1609s	
[3-AcetPyH]$_2$[CoCl$_4$]		2325s	1688vs	1598s	301vs 285sh 275sh
[3-AcetPyH]$_2$[NiCl$_4$]3H$_2$O	3370m	2425s 2280m 2118m	1693vs	1598s	250vs 230sh
[3-AcetPyH]$_2$[CuCl$_4$]		2255s 2223m	1693vs	1593s	291sh 280vs 240sh
4-AcetPyH$^+$Cl$^-$		2355sh 2335s 2175sm	1705vs	1603s	
[4-AcetPyH]$_2$[CoCl$_4$]		2300s	1695vs	1592s	298vs 275m
[4-AcetPyH]$_3$[NiCl$_5$]		2380s	1706vs	1601m	260s 222s
[4-AcetPyH]$_n$(CuCl$_3$)$_n$nH$_2$O	3380sh 3320m, b	2360s	1700vs	1595s	278m 264s 255m 228s

the cobalt salts. As with the 4-acetylpyridinium salt of the chloronickelate(II) ion, the cuprate salt of this cation is different; the analyses show only a 3:1 ratio of chloride to copper rather than 4:1. We have based our proposed stereochemistry on the rather low energies of the ν_{Cu-Cl} bands which suggest that the anion is polymeric, although other spectroscopic evidence will be considered later concerning this assignment. Thermal properties of this salt are rather complex, and the TGA studies show loss of two moles of H$_2$O (calcd, 5.2%; found, 5.5%) at *ca.* 105 °C. The weight loss at 170 °C is consistent with loss of two moles of 4-acetylpyridine (calcd, 39%; found, 38.7%).

The metal–chlorine stretching frequencies and the other bands useful in establishing the nature of these solids are compiled in Table II. Both of the solids that were isolated containing molecules of water have broad bands for ν_{O-H} consistent with the assignment of lattice water rather than coordinated water. In addition, division of the enthalpy change by the number of water molecules lost gives a value of *ca.* 7 kcal/mol showing the similar role of water in these two solids. In all the solids involving chlorometallate ions the $\nu_{C=O}$ of the cation is not significantly shifted from its position in the spectra of the corresponding chloride salts. But with the 2-acetylpyridine complexes mentioned earlier this band is shifted some 50–80 cm^{-1} lower in energy because of coordination of the carbonyl oxygen.

The two infrared bands useful in determining the extent of hydrogen bonding to the chlorines of the chlorometallates as well as the chloride ions are also included in Table II. When the spectra of substituted ammonium chlorides and the analogous ammonium tetrachlorocuprates(II) were compared, the ν_{N-H} was found to undergo a positive shift of 250–300 cm^{-1} for the latter salts [10]. A comparable shift would be expected for the pyridinium proton in these salts as measured by changes in ν_{py-H^+} and $\nu_{C=N^+}$. However, for the aminopyridinium salts little difference in these bands was observed when the chlorides and the chlorocuprates(II) were compared [4]. When the amino group was present on the ring it was thought that its hydrogens, as well as the pyridinium hydrogen, might be involved in bonding. The shifts of the above bands in the opposite direction compared to the analogous bands for the ammonium salts were rationalized in terms of reduced competition for hydrogen bonding in the larger $CuCl_4^{2-}$, which has more sites for hydrogen bonding. Included in that report [4] was picolylchloride hydrochloride and its corresponding tetrachlorocuprate(II) salt, and no differences in the positions of these two bands were observed in the spectra of the two salts. Therefore, it is not particularly surprising that in the present solids there is little difference between the two types of salts apparently owing to stronger hydrogen bonding involving the larger anions and, therefore, an opposite trend to the ammonium salts. Again, the greater number of sites as well as steric factors reducing the hydrogen bonding in the chloride salts are probably the principle reasons for this effect.

The three tetrachlorocobaltate(II) salts show a very strong absorbance at *ca.* 300 cm^{-1} which is assignable to a ν_{Co-Cl} band of an essentially tetrahedral Co(II) species [11]. In addition, one or two other bands found as shoulders at lower energy have been assigned as having considerable cobalt–chlorine stretching character, and these bands would arise from the distortion in bond angles and bond lengths due to hydrogen bonding. The ν_{Ni-Cl} bands have been considered earlier in this report, and it need only be noted that both solids have these bands at considerably lower energy than the 320 cm^{-1} found for pseudotetrahedral $NiCl_4^{2-}$ [11].

Most tetrachlorocuprates(II) reported on to date have been found to be of D_{2d} symmetry which yields two ν_{Cu-Cl} bands (e and b_2) or three bands if the e mode is split. For example, with piperidinium and piperazinium salts [12] the e mode of $CuCl_4^{2-}$ showed bands at 290–295 cm^{-1} and 262–279 cm^{-1}, with the b_2 stretching mode at 230 cm^{-1}. For $[3\text{-AcetPyH}]_2[CuCl_4]$ the two bands of the e mode are resolved, and it should be noted that these bands are at somewhat higher energy than those found for the chlorocuprate(II) salts of, for example, the 2-aminopyridinium cation (281sh, 274s and 272s). This is probably because of the diminished hydrogen bonding in the present cation due to the absence of the amine group. We assign the b_2 mode to the shoulder at 240 cm^{-1}. Also the chlorocuprate salt isolated with 4-AcetPyH^+ shows bands at much lower energy than usually observed for a tetrachlorocuprate(II) ion and may involve bridging chlorides, a higher coordination number, or both. Estes *et al.* [13] have shown that $Cu_2Cl_6^{2-}$ ions range from quasi-planar to distorted tetrahedral depending on the size of the cations, the latter geometry favored by large cations. However, these ions commonly have their lowest energy d–d transition at 8.0–9.0 kK [13] for distorted tetrahedral $Cu_2Cl_6^{2-}$ and have values of 10.5–11.0 [14] for quasi-planar $Cu_2Cl_6^{2-}$. In addition, a band at *ca.* 19.0 kK due to a π-dimer transition [14] which gives the characteristic orange-red color to $Cu_2Cl_6^{2-}$ is not present in our spectrum. The bridging chlorines have ν_{CuCl} at 228 cm^{-1} and terminal chlorines are assignable to the remaining three bands. The latter energies are lower than normal due to the involvement of the terminal chlorines in hydrogen bonding.

For the three tetrachlorocobaltates(II) there are a number of bands which appear as shoulders on higher energy bands due to electronic transitions of the acetylpyridinium cations. These we have listed as 'other bands'. Day and Jorgensen [15] have recorded the charge transfer spectra of both $CoCl_4^{2-}$ and $NiCl_4^{2-}$, and their results indicate that the lowest energy ligand-to-metal charge transfer band would be expected at 42 kK and 36 kK for Co(II) and Ni(II), respectively. Therefore, the bands found in the 20–28 kK region of the spectrum for the various Co(II) and Ni(II) salts of this study are also likely due to electronic transitions of the cations. Calculation [16] of an optical electronegativity value for Cl^-, based on a band at *ca.* 28 kK being a Cl → Co(II) charge transfer, gives a value of 2.6, which is much lower than the expected 3.0 [15].

Whereas previous workers were able to assign as many as five charge transfer bands for D_{2d} $CuCl_4^{2-}$, the strong $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the pyridinium ring and the acetyl group obscure all but the lowest energy bands (*i.e.*, Cl to Cu(II)). The two bands observed for the 3-AcetPyH^+ salt are of similar energy to those found for the aminopyridinium salts [4]. The existence of a single band for the 4-Acet salt is probably more a function of the difficulty of observing this type of band which appears as a shoulder on a stronger intraligand band rather than the possibility that a single band exists.

In Table IV band assignments and ligand field calculations are shown for the three $CoCl_4^{2-}$ salts. There is good agreement between the values for the three salts as well as with the value Dq = 350 cm^{-1} reported by Holm and Cotton for the quinolinium salt [17]. The lowest value calculated for the 4-acetyl salt may be an indication not only of its hydrogen bonding but that this cation requires greater space in the crystal lattice and thus has greater deviation from tetrahedral symmetry. Also included in Table IV are the calculations for Dq and B for the 3-Acetyl salt of $NiCl_4^{2-}$, and they correspond well with the values of 409 and 791 cm^{-1} reported for a non-hydrogen bonded anion [18]. Though some 5-coordinate complexes of Ni(II) are known, they tend to result from stereochemical requirements of the ligand and are somewhat uncommon. While our result is surprising, the electronic spectrum does not resemble either that of a tetrahedral or octahedral complex.

Our assignments of the ν(d–d) bands to the D_{2d} levels $^2B_2 \rightarrow {}^2E$ *etc.* for $CuCl_4^{2-}$ are included in Table

TABLE III. Electronic Spectra (kK) of Some Acetylpyridinium Salts of Chlorometallates and the Powder Esr Spectra Parameters of the Chlorocuprates(II).

Co(II) Compounds	$\nu_2(^4A_2 \rightarrow {}^4T_1(F))$	$\nu_3(^4A_2 \rightarrow {}^4T_1(p))$	Other Bands
$[2\text{-AcetPyH}]_2[CoCl_4]$	5.79	15.43sh 14.56 14.04sh	27.78sh 21.51 18.25
$[3\text{-AcetPyH}]_2[CoCl_4]$	6.12	15.85sh 14.97 14.49sh	29.40sh 22.27 18.87
$[4\text{-AcetPyH}]_2[CoCl_4]$	5.82	15.02sh 14.08 13.61sh	26.32sh 20.83 17.54
Ni(II) Compounds	d–d Bands		Other Bands
$[3AcetPyH]_2[NiCl_4]\cdot 3H_2O$	6.85($^3T_1 \rightarrow {}^3A_2$); 11.83($^3T_1 \rightarrow {}^1E$); 13.74, 14.62($^3T_1 \rightarrow {}^3T_1(p)$; 18.52($^3T_1 \rightarrow {}^1T_2$)		21.19, 23.42
$[4AcetPyH]_3[NiCl_5]$	6.85sh, 7.69, 11.49sh, 13.66		21.14sh, 23.26sh 27.25sh
Cu(II) Compounds	d–d Bands		C.T Bands
	$^2B_2 \rightarrow {}^2E$ $^2B_2 \rightarrow {}^2B_1$ $^2B_2 \rightarrow {}^2A_1$		
$[3AcetPyH]_2[CuCl_4]$	8.06, 10.64, 12.22		20.00sh, 26.45sh
298 K:	$g_{\parallel} = 2.330$	$g_{\perp} = 2.066$	$g_{av} = 2.154$
77 K:	$g_{\parallel} = 2.316$	$g_{\perp} = 2.059$	$g_{av} = 2.145$
$[4AcetPyH]_n(CuCl_3)_n\cdot nH_2O$	(6.58) 11.63, 14.45sh		25.64sh
298 K:	$g_{\parallel} = 2.284$	$g_{\perp} = 2.066$	$g_{av} = 2.139$
77 K:	$g_{\parallel} = 2.254$	$g_{\perp} = 2.069$	$g_{av} = 2.131$

TABLE IV. d–d Assignments and Approximate Ligand Field Parameters (cm^{-1}).

Co(II) Compounds	$\nu_2(^4A_2 \rightarrow {}^4T_1(F))$	$\nu_3(^4A_2 \rightarrow {}^4T_1(P))$	ν_1(Calcd)	Dq	B
$[2AcetPyH]_2CoCl_4$	5790	14,660	3340	334	697
$[3AcetPyH]_2CoCl_4$	6120	14,840	3530	353	690
$[4AcetPyH]_2CoCl_4$	5820	14,200	3010	301	661
Ni(II) Compounds	$\nu_2(^3T_1 \rightarrow {}^3A_2)$	$\nu_3(^3T_1 \rightarrow {}^3T_1(P))$	ν(calcd)	Dq	B
$[3AcetPyH]_2NiCl_4\cdot 3H_2O$	6850	14,180	3312	373	775

III. A number of different proposals have been made for correlating the energy of the d–d transitions with a distortion parameter [19, 20]. These methods involved the highest energy d–d band and were reasonably successful in showing a meaningful trend. However, inclusion of the esr powder results and calculation of the covalency parameters to check the validity of the assignment of the three bands led to the fitting of these bands with more extensive theoretical calculations [4]. The crystal field equations first reported by Karipides and Piper [21] were employed and the results correlated with those reported more recently by other authors [22]. A plot of d–d band energies (kK) *versus* the distortion angle (β) for various tetrachlorocuprate(II) salts of pyridinium ions as well as ammonium ion salts reported by others [12, 23] proved an excellent fit, and therefore prediction of the distortion angle from the solid state spectra [4] is possible. Fitting the bands for the 3-acetyl salt to this same figure yields an approximate value of 73 °C and is in agreement with the greater planarity of the $CuCl_4^{2-}$ for this yellow-green salt. Values for the covalency parameters $k^2_{\parallel} = 0.53$ and $k^2_{\perp} = 0.31$ are similar to the values calculated for the previous substituted pyridinium salts [4]. The roots of $k_{\parallel} = 0.73$ and $k_{\perp} = 0.56$ are indicative of significant out of plane π-bonding ($k_{\parallel} > k_{\perp}$) [23].

While the 4-acetyl salt formed with chlorocuprate ion might have been a $Cu_2Cl_6{}^{2-}$ ion, the electronic spectrum is not consistent with that formulation. Further, the resolved esr spectrum of a monomeric $d_{x^2-y^2}$ ground state Cu(II) ion is also inconsistent with that assignment [13], although the signal could be due to a rather planar $CuCl_4{}^{2-}$ impurity. Lacking any crystal structure data, we cannot at this time speculate further on the nature of this solid.

Acknowledgement

This work was supported in part by the U.S. Air Force Office of Scientific Research.

References

1 D. W. Smith, *Coord. Chem. Rev., 21,* 93 (1976) and references therein.
2 A. Doadrio, D. Craciunescu and J. Shohet, *An. Quin., 71,* 49 (1975).
3 D. Carciunescu, A. Doadrio and C. Ghirvu, *Z. Phys. Chem. (Leipzig), 257,* 97 (1976).
4 R. M. Gaura, P. Stein, R. D. Willett and D. X. West, *Inorg. Chim. Acta, 60,* 213 (1982).
5 F. A. Cotton and R. Francis, *J. Am. Chem. Soc., 82,* 2986 (1960).
6 J. R. Ferraro and A. T. Sherren, *Inorg. Chem., 17,* 2498 (1978).
7 L. P. Battaglia, A. Bonamartini Corradi, G. Marcotrigiano, L. Menabue and G. C. Pellacani, *Inorg. Chem., 21,* 3919 (1982).
8 D. X. West and W.-H. Wang, *J. Inorg. Nucl. Chem., 41,* 1719 (1979); *43,* 1511 (1981).
9 Y. Kidani, M. Noji and H. Koike, *Bull. Chem. Soc. Japan, 48,* 239 (1975).
10 G. W. Watt and W. J. Wells, Jr., *J. Inorg. Nucl. Chem., 38,* 921 (1976).
11 B. S. Bloodworth, B. Demetriou and R. Grziskowiak, *Inorg. Chim. Acta, 34,* L197 (1979).
12 G. Marcotrigiano, L. Menabue, G. C. Pellacani and M. Saladini, *Inorg. Chim. Acta, 34,* 43 (1979).
13 W. E. Estes, J. R. Wasson, J. W. Hall and W. E. Hatfield, *Inorg. Chem., 17,* 3657 (1978).
14 R. O. Willett and O. L. Liles, Jr., *Inorg. Chem., 6,* 1666 (1967).
15 P. Day and C. K. Jorgensen, *J. Chem. Soc.,* 6226 (1964).
16 W. Byers, B. Fa-Chun Chou, A. B. P. Lever and R. V. Parish, *J. Am. Chem. Soc., 91,* 1329 (1969).
17 R. H. Holm and F. A. Cotton, *J. Chem. Phys., 31,* 788 (1959).
18 M. Goodgame, D. M. L. Goodgame and F. A. Cotton, *J. Am. Chem. Soc., 83,* 4161 (1961).
19 R. L. Harlow, W. J. Wells, III, G. W. Watt and S. H. Simonsen, *Inorg. Chem., 13,* 2106 (1974).
20 R. D. Willett, J. A. Haugen, J. Lebsack and J. Morrey, *Inorg. Chem., 13,* 2510 (1974).
21 A. G. Karipides and T. S. Piper, *Inorg. Chem., 1,* 970 (1962).
22 E. J. Soloman, J. W. Hare, D. W. Dooley, J. H. Dawson, P. J. S. Stephens and H. B. Gray, *J. Am. Chem. Soc., 102,* 168 (1980).
23 J. R. Wasson, J. W. Hall, H. W. Richardson and W. E. Hatfield, *Inorg. Chem., 16,* 458 (1977); P. Cassidy and M. A. Hitchman, *Inorg. Chem., 16,* 1568 (1977); and J. Ferguson, *J. Chem. Phys., 40,* 3406 (1964).
24 R. S. Naidu and R. R. Naidu, *J. Inorg. Nucl. Chem., 41,* 1625 (1979).