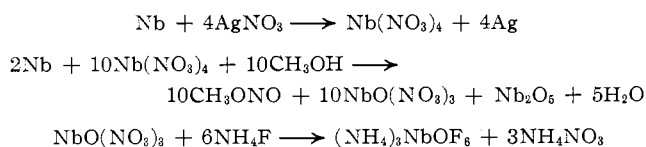
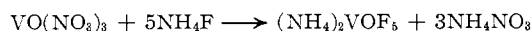


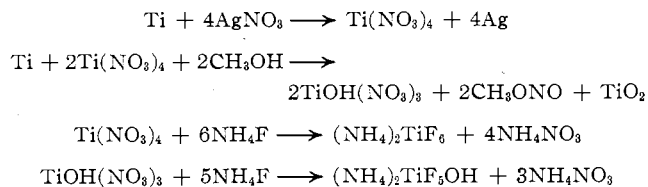
characteristic of the precipitated fluoride, the following sequence of reactions is proposed: For niobium



For vanadium, the first two steps are as for niobium, followed by



For titanium



The postulation of $\text{NbO}(\text{NO}_3)_3$ as an intermediate is reasonable. A recent paper¹¹ indicates that the compound has been prepared and that it reacts with potassium fluoride to give K_3NbOF_6 . We have also shown¹² that a bromide, prepared in methanol but not isolated, reacts with methanolic ammonium fluoride to give $(\text{NH}_4)_3\text{NbOF}_6$. A similar argument can be applied to the case of vanadium, although the corresponding $\text{VO}(\text{NO}_3)_3$ has not yet been isolated.

The existence of titanium(IV) nitrate in solution is less definite, and the evidence for the formation of the hydroxy nitrate is inferential. The formation of methyl nitrite must be accompanied by solvent oxidation or the introduction of oxygen into the titanium species by some oxidative mechanism. It does not seem reasonable, however, to assume that oxide ion can be present in the fluoride derivative without substantially altering the X-ray diffraction pattern from the $(\text{NH}_4)_2\text{TiF}_6$ type. Hydroxyl can substitute isomorphously for fluoride without an alteration in the observed powder pattern.

(11) B. O. Field and C. J. Hardy, *Proc. Chem. Soc.*, 11 (1963).

(12) A. E. Baker and H. M. Haendler, *Inorg. Chem.*, 1, 127 (1962).

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Charge-Transfer Spectra Involving Anions Outside the Coordination Sphere

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Received December 14, 1964

The existence of charge-transfer bands in the electronic spectra of coordination compounds is now well established. Depending upon the formal charge on

the metal and the nature of the ligands, such bands may involve either the "oxidation" or the "reduction" of the metal ion.¹ In most known cases of charge-transfer bands in coordination compounds, the group involved in the transfer is coordinated to the metal.

Examples in which the group involved is not coordinated to the metal are less common. Linhard² has observed that a very intense ultraviolet band that appears in solutions of $\text{Co}(\text{NH}_3)_6^{3+}$ shifts to lower energies upon the addition of bromide or iodide ion. He attributes this to charge transfer between the anion and the complex cation. We wish to report here two series of compounds in which charge transfer involving anions outside the coordination sphere may be responsible for the observed spectra of the solids.

Experimental

Materials.—The synthesis of $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ was accomplished by the method of Burstall and Nyholm.³ In this procedure anhydrous chromium(III) chloride and the required amount of bipyridyl are dissolved in hot methanol and a trace of zinc dust is added. Upon cooling, a green substance precipitates, and after recrystallization from water, brown $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ is obtained. *Anal.* Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_3\text{Cr}\cdot 2\text{H}_2\text{O}$: C, 47.40; H, 3.95; N, 11.06. Found: C, 47.79; H, 4.18; N, 10.89.

The salts $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{X}\cdot 2\text{H}_2\text{O}$ ($\text{X} = \text{Br}^-$, N_3^-) and $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{X}$ ($\text{X} = \text{I}^-$, SCN^-) were prepared by dissolving $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{Cl}\cdot 2\text{H}_2\text{O}$ in warm water and adding an aqueous solution of the sodium salt of the appropriate anion. The different salts immediately precipitated. *Anal.* Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_2\text{BrCr}\cdot 2\text{H}_2\text{O}$: C, 43.55; H, 3.66; N, 10.17. Found: C, 43.75; H, 3.92; N, 10.07. Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_7\text{Cl}_2\text{Cr}\cdot 2\text{H}_2\text{O}$: C, 46.76; H, 3.93; N, 19.10. Found: C, 46.9; H, 3.38; N, 19.4. Calcd. for $\text{C}_{20}\text{H}_{16}\text{N}_4\text{Cl}_2\text{ICr}$: C, 42.74; H, 2.87; N, 9.97. Found: C, 42.13; H, 2.88; N, 10.06. Calcd. for $\text{C}_{21}\text{H}_{16}\text{N}_6\text{Cl}_2\text{SCr}$: C, 51.1; H, 3.27; N, 14.20. Found: C, 50.91; H, 3.29; N, 14.70.

X-Ray powder data showed the three dihydrates (Cl^- , Br^- , N_3^-) to be isomorphous as were the two anhydrous salts (I^- , SCN^-). The colors of the salts were distinctly different, being for the chloride, bromide, and azide different shades of green, for the iodide yellow, and for the thiocyanate light brown.

The preparation of $[\text{Cr}(\text{phen})_2\text{Cl}_2]\cdot 2\text{H}_2\text{O}$ followed exactly that of the analogous bipyridyl complex with the substitution of 1,10-phenanthroline for the bipyridyl. The product recovered from the methanol, however, was red in color and analysis indicated that the recovered product was approximately the 4-hydrate. *Anal.* Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cl}_2\text{Cr}\cdot 4\text{H}_2\text{O}$: C, 48.79; H, 4.09; N, 9.48. Found: C, 49.42; H, 3.59; N, 9.30.

The salts $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{X}\cdot 4\text{H}_2\text{O}$ ($\text{X} = \text{Br}^-$, N_3^- , SCN^-) and $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{I}\cdot 2\text{H}_2\text{O}$ were precipitated from a warm aqueous solution of the chloride by the addition of the appropriate sodium salt. *Anal.* Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cl}_2\text{BrCr}\cdot 4\text{H}_2\text{O}$: C, 45.43; H, 3.78; N, 8.83. Found: C, 45.74; H, 3.63; N, 8.67. Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_7\text{Cl}_2\text{Cr}\cdot 4\text{H}_2\text{O}$: C, 48.24; H, 4.02; N, 16.42. Found: C, 48.05; H, 3.84; N, 16.36. Calcd. for $\text{C}_{25}\text{H}_{16}\text{N}_6\text{Cl}_2\text{SCr}\cdot 4\text{H}_2\text{O}$: C, 48.94; H, 3.92; N, 11.42. Found: C, 49.54; H, 3.52; N, 12.12. Calcd. for $\text{C}_{24}\text{H}_{16}\text{N}_4\text{Cl}_2\text{ICr}\cdot 2\text{H}_2\text{O}$: C, 44.58; H, 3.10; N, 8.67. Found: C, 44.54; H, 3.35; N, 9.37.

Again the X-ray powder data show that all the 4-hydrates (Br^- , N_3^- , SCN^- , red Cl^-) are isomorphous. The colors of the

(1) See, for example, L. E. Orgel, "An Introduction to Transition Metal Chemistry," John Wiley and Sons, New York, N. Y., 1960, Chapter 6.

(2) M. Linhard, *Z. Elektrochem.*, 50, 224 (1944).

(3) F. H. Burstall and R. S. Nyholm, *J. Chem. Soc.*, 3577 (1952).

salts were, for the iodide and azide, orange-brown, for the bromide, maroon, and for the thiocyanate, light tan.

Spectra.—Solution spectra were obtained in a 50–50 methanol–water solution using a Perkin-Elmer Model 4000A spectrophotometer and 1-cm. cells. The spectra of the solids were obtained by reflectance using a Beckman DU equipped with a standard reflectance attachment.

Discussion

The reflectance spectra for the two series of compounds $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{X}\cdot n\text{H}_2\text{O}$ and $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{X}\cdot n\text{H}_2\text{O}$ are given in Figures 1 and 2. They consist of

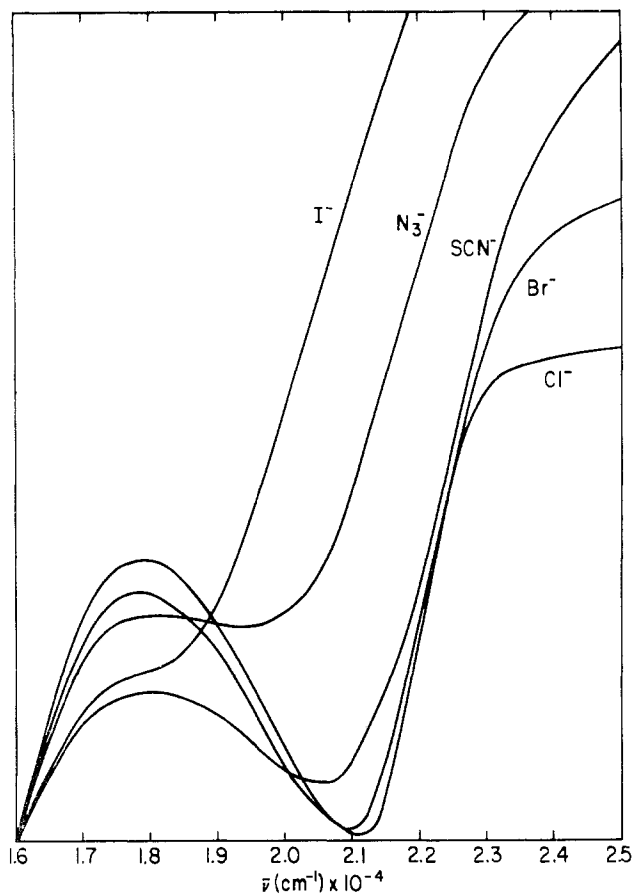


Figure 1.—Reflectance spectra of $[\text{Cr}(\text{phen})_2\text{Cl}_2]\text{X}\cdot n\text{H}_2\text{O}$. The ordinate is relative intensity only.

two main features, a rather weak band at about $18,000\text{ cm}^{-1}$ and the beginning of a much more intense band at higher energies.

For both series of compounds, the band at $18,000\text{ cm}^{-1}$ can be assigned as a d–d transition, specifically ${}^4A_{2g} \rightarrow {}^4T_{2g}$. As would be expected, the energy of this band in the phenanthroline series is, as near as can be determined, independent of the anion. For the bipyridyl series, however, the iodide and thiocyanate transitions occur at noticeably higher energies than the other three. It is interesting that these two are anhydrous while the other three are dihydrates. Why the water of hydration should cause this difference in the d–d band is not clear.

The solution spectra for the five compounds in each series are identical, with the low-energy band appearing at $18,000\text{ cm}^{-1}$ for the bipyridyls and at $17,800\text{ cm}^{-1}$

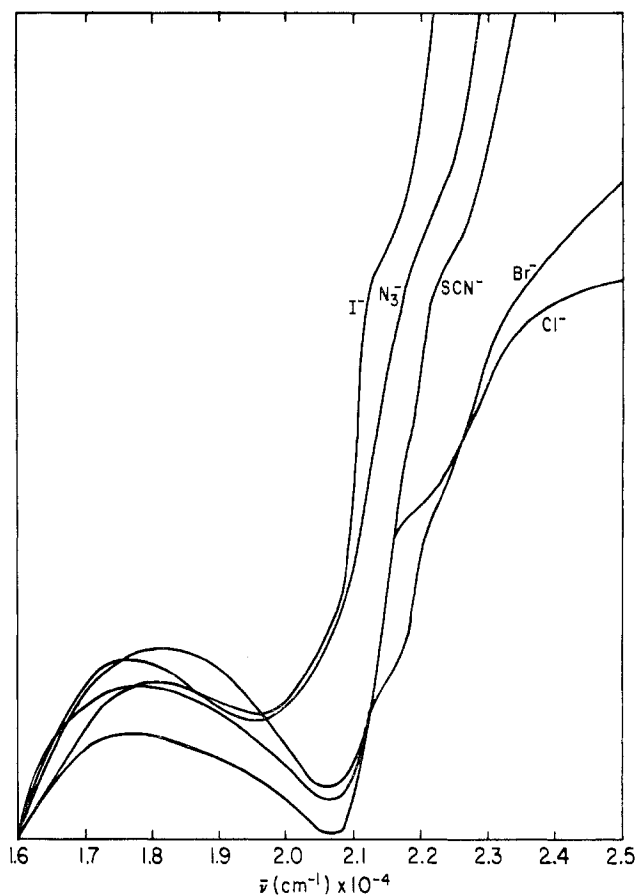


Figure 2.—Reflectance spectra of $[\text{Cr}(\text{bipy})_2\text{Cl}_2]\text{X}\cdot n\text{H}_2\text{O}$. The ordinate is relative intensity only.

for the phenanthrolines. Furthermore, the compounds can be repeatedly dissolved and precipitated without changing either the solution or solid spectra. This is cited only as additional evidence that in all cases two chloride ions are coordinated and the variable anion is not.

The portion of the spectrum of interest is the intense absorption beginning at higher energies. The intensity of the band indicates that it is due to an allowed transition and it is clear that the energy depends on the nature of the anion, especially for the compounds in the phenanthroline series. The order of energies of the bands for both series is the same, $\text{I}^- < \text{N}_3^- < \text{SCN}^- < \text{Br}^- < \text{Cl}^-$. This order is the same as found by Linhard, *et al.*,⁴ for the charge-transfer bands in the series $[\text{Cr}(\text{NH}_3)_5\text{X}]^{2+}$, $\text{X} = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{N}_3^-, \text{and } \text{SCN}^-$. All of this suggests that the high-intensity bands observed in our compounds are charge transfer in nature and either directly or indirectly involve the anion outside the coordination sphere.

Charge-transfer bands of this type undoubtedly appear in the spectra of other complexes, but the effect is particularly striking here because the bands extend into the visible region and thus affect the color of the compounds (see Experimental section). The fact that the effect of the anions is so pronounced in these

(4) M. Linhard, H. Siebert, and M. Weigel, *Z. anorg. allgem. Chem.*, **278**, 287 (1955).

complexes is probably due to the conjugated nature of the phenanthroline and bipyridyl which in some way leads to a greater electronic interaction with the anions.

Acknowledgment.—The support of the National Science Foundation is gratefully acknowledged.

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The Crystal and Molecular Structure of Tetramethylammonium Hexahydrohexaborate¹

BY RILEY SCHAEFFER,² QUINTIN JOHNSON, AND GORDON S. SMITH

Received December 17, 1964

Eberhardt, *et al.*, have explicitly pointed out that a $B_6H_6^{2-}$ ion of octahedral symmetry can be well-described by a closed-shell electronic structure.³ In less explicit fashion, the treatment of MB_6 borides by Longuet-Higgins and Roberts leads to a similar conclusion, since the internal electronic structure is undisturbed if the external B–B bonds linking octahedra in the boride structure are replaced by external B–H bonds.⁴ Recent isolation by Boone of salts containing the $B_6H_6^{2-}$ ion makes it possible to confirm this structure.⁵ We have now carried out a complete X-ray structure analysis of tetramethylammonium hexahydrohexaborate.

The powder pattern can be indexed on the basis of a face-centered cubic lattice with $a = 11.84 \pm 0.01 \text{ \AA}$., suggesting a gross structure of the m_2x salt based on the antifluorite structure. The calculated density, assuming four molecules per unit cell, is 0.89 g. cm.^{-3} compared with $0.88 \pm 0.02 \text{ g. cm.}^{-3}$ measured by Boone.

Crystals grown from water solution were examined by precession and Weissenberg methods. Systematic extinctions are consistent with space groups $F432$, $F\bar{4}3m$, and $Fm3m$. The intensities of 59 independent reflections were measured with $M\alpha K\alpha$ radiation ($\lambda 0.7107 \text{ \AA}$.) on a G.E. XRD-5 diffractometer equipped with a single-crystal orienter.

The structure was solved by noticing that the antifluorite structure can accommodate the octahedral $B_6H_6^{2-}$ ion at the origin and the tetrahedral (disregarding hydrogen) $N(CH_3)_4^+$ ion at $\pm 1/4, 1/4, 1/4$. Reasonable values for the two parameters which relate to the size of the ions can be guessed from expected bond distances. Preliminary structure factor calculations verified this model.

(1) Studies of Boranes. XVI. For paper XV of this series see J. Dobson and R. Schaeffer, *Inorg. Chem.*, **4**, 593 (1965).

(2) Department of Chemistry, Indiana University, Bloomington, Ind.

(3) W. H. Eberhardt, B. L. Crawford, Jr., and W. N. Lipscomb, *J. Chem. Phys.*, **22**, 989 (1954).

(4) H. C. Longuet-Higgins and M. de V. Roberts, *Proc. Roy. Soc. (London)*, **A224**, 336 (1954).

(5) J. Boone, *J. Am. Chem. Soc.*, **86**, 5036 (1964).

From a difference Fourier based on this structure, the boron-bonded hydrogen atom was readily located, but the methyl hydrogens gave the appearance of free rotation. As an approximation to free rotation, half-hydrogen atoms were introduced in 192-fold general positions of space group $Fm3m$. Least-squares refinements yielded bond distances as well as temperature factors that were unacceptable. The resolution of the difference Fourier was poor because only a small amount of data were available. If the methyl hydrogen atoms were fixed, but had a large thermal parameter, the appearance would probably be one of free rotation; therefore, two alternate structures in this space group were considered in which hydrogen atoms were fixed. These structures, which have hydrogen atoms located in mirror planes, differ by a 60° rotation of the methyl group. One structure resulted in no improvement over free rotation, but the other structure gave realistic bond distances and temperature factors as well as a substantial improvement in the R factor.

This structure, with anisotropic temperature factors for boron and carbon, was refined by a full-matrix, least-squares program until the parameter shifts were less than one-tenth of the estimated standard deviation.⁶ The final R factor was 5.3%. As an approximation to a weighting scheme appropriate for diffractometric data,⁷ the following was used: $W = F_o^{1/4}$ for $F_o < A$, $W = A^{5/4}F_o^{-1}$ for $F_o > A$. Scaled to the structure factor data in Table II, A is 6.

Final parameters for all atoms are shown in Table I. The notation is that of "International Tables for X-ray Crystallography," Vol. I.⁸ Observed and calculated structure factors are shown in Table II and pertinent bond distances are given in Table III.

Powder photographs, using chromium radiation ($\lambda K\alpha_1 2.28963 \text{ \AA}$.), of the corresponding cesium salt show a pseudo-primitive cubic cell, $a = 4.78 \text{ \AA}$., due to the overwhelming scattering of cesium. Weak lines require the true cell to be a face-centered cubic lattice with $a = 9.561 \pm 0.001 \text{ \AA}$. Isomorphism with the tetramethylammonium salt would appear likely.

TABLE I
FINAL ATOMIC PARAMETERS FOR $[N(CH_3)_4]_2B_6H_6$

24	B	(e)	$x = 0.1007 \pm 0.0008$ $\beta_{11} = 0.0071 \pm 0.0010$ $\beta_{22} = 0.0088 \pm 0.0006$
32	C	(f)	$x = 0.3219 \pm 0.0004$ $\beta_{11} = 0.0137 \pm 0.0005$ $\beta_{12} = -0.0065 \pm 0.0009$
8	N	(c)	$B = 3.9 \pm 0.3 \text{ \AA}^2$
24	H ₁	(e)	$x = 0.194 \pm 0.006$ $B = 3.3 \pm 1.8 \text{ \AA}^2$
96	H ₂	(m)	$x = 0.368 \pm 0.003$ $z = 0.269 \pm 0.004$ $B = 8.7 \pm 1.5 \text{ \AA}^2$

(6) Unpublished ACA Program No. 317 by Gantzel, Sparks, and Trueblood.

(7) G. S. Smith and L. E. Alexander, *Acta Cryst.*, **16**, 462 (1963).

(8) "International Tables for X-ray Crystallography," Vol. I, The Kynoch Press, Birmingham, 1952.