

- (12) A. Zalkin, University of California; modified by B. Foxman, Massachusetts Institute of Technology.
- (13) C. T. Prewitt, Ph.D. Thesis, Massachusetts Institute of Technology, 1962, p 163, modified by B. Foxman and M. J. Bennett, Massachusetts Institute of Technology, 1967.
- (14) W. C. Hamilton, Brookhaven National Laboratory, Upton, N.Y.
- (15) W. Busing and H. A. Levy, Report ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.
- (16) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.
- (17) J. S. Valentine, *Chem. Rev.*, **73**, 235 (1973).
- (18) M. J. Nolte, E. Singleton, and M. Laing, *J. Am. Chem. Soc.*, **97**, 6396 (1975).
- (19) M. Calligaris, G. Nardin, L. Randaccio, and A. Ripamonti, *J. Chem. Soc.*, **A**, 1069 (1970).
- (20) R. E. Marsh and W. P. Schaefer, *Acta Crystallogr., Sect. B*, **24**, 246 (1968).
- (21) R. H. Jackson, *J. Chem. Soc.*, 4585 (1962).
- (22) M. J. Barrow and O. S. Mills, *J. Chem. Soc. A*, 864 (1971).
- (23) J. S. Griffith, *Proc. R. Soc. London, Ser. A*, **23**, 235 (1956).
- (24) A. C. Wahl, *Science*, **151**, 961 (1966).
- (25) L. Sutton and L. O. Brockway, *J. Am. Chem. Soc.*, **57**, 473 (1935).
- (26) R. J. Myers and W. D. Gwinn, *J. Chem. Phys.*, **20**, 1420 (1952).
- (27) M. J. Bennett and P. B. Donaldson, *Inorg. Chem.*, **16**, 655 (1977).
- (28) P. B. Hitchcock, M. McPartlin, and R. Mason, *J. Chem. Soc., Chem. Commun.*, 1367 (1969).
- (29) M. Nolte, E. Singleton, and M. Laing, *J. Chem. Soc., Dalton Trans.*, **19**, 1979 (1976).
- (30) A referee has suggested describing the molecule in terms of two idealized methylene chloride molecules. Unfortunately facilities for attempting this were not available.
- (31) R. Hoffmann, M. M.-L. Chen, and D. L. Thorn, *Inorg. Chem.*, **16**, 503 (1977).
- (32) B. Teo and W. Li, *Inorg. Chem.*, **15**, 2005 (1976).

Contribution from the Department of Crystallography (No. 282)  
and the Department of Chemistry, University of Berne, Berne, Switzerland

## Crystal Structure and Polarized Electronic Spectrum of $\mu$ -Hydroxo-bis[pentaaminechromium(III)] Chloride Dihydrate

PETER ENGEL and HANS U. GÜDEL\*

Received November 20, 1976

AIC608340

The crystal structure of  $\mu$ -hydroxo-bis[pentaaminechromium(III)] chloride dihydrate has been determined from three-dimensional x-ray diffractometer data. The compound crystallizes in the monoclinic space group  $C2/c$  with  $a = 23.656$  (9) Å,  $b = 7.36$  (1) Å,  $c = 16.718$  (8) Å, and  $\beta = 128.1$  (1)°. Least-squares refinement of 1112 independent reflections led to a final  $R$  value of 0.091. The dimeric  $[(\text{NH}_3)_5\text{CrOHCr}(\text{NH}_3)_5]^{3+}$  complexes are oriented with their twofold axes parallel to the  $b$  axis of the unit cell. Single-crystal absorption spectra in the region of single pair excitations  ${}^4A_{2g} \rightarrow {}^4A_{2g} \rightarrow {}^4A_{2g} \rightarrow {}^4E_g$ ,  ${}^4A_{2g} \rightarrow {}^4T_{1g}$  have been measured down to liquid helium temperatures. The structural and spectroscopic informations are combined to determine the polarizations of the optical transitions with respect to the symmetry axes of the dinuclear complexes. There are at least two intensity-gaining mechanisms active in this region. The most prominent absorption bands are shown to arise through an exchange-induced mechanism.

### Introduction

Exchange interactions in the classical dinuclear rhodo and erythro chromium(III) complexes have been studied by magnetic susceptibility measurements as well as spectroscopic methods.<sup>1-4</sup> The spectroscopic investigations have been hampered somewhat by a lack of crystal structure information. Two crystal structure determinations of acid rhodo chloride monohydrate have been reported, but neither of the published structures<sup>2,5</sup> is compatible with the results of a spectroscopic study.<sup>4</sup>

The information gained by single-crystal absorption or emission spectroscopy can only partly be used if the orientation of the dinuclear complexes with respect to the optical extinction directions of the crystal is unknown. A knowledge of the polarizations of pair transitions with respect to the symmetry axes of the complex is particularly important if one is interested in the mechanisms by which those transitions gain their intensity. Several intensity-gaining mechanisms have been found to be operative in chromium(III) pair transitions. As in mononuclear complexes, spin-forbidden electric dipole transitions may arise through combined action of spin-orbit coupling and odd-parity crystal field. Pair transitions due to this single-ion mechanism have been found in the spectrum of ruby.<sup>6</sup> At least part of the intensity of the spin-forbidden bands in trigonal  $\text{Cs}_2\text{Cr}_2\text{Br}_9$  appears to be due to this mechanism.<sup>7</sup> Another possibility for spin-forbidden transitions in dinuclear complexes to gain intensity is through an exchange-induced electric dipole mechanism first proposed by Tanabe.<sup>8</sup> Some of the most prominent bands in the chromium(III)-pair spectra of  $\text{Al}_2\text{O}_3$ ,<sup>6</sup>  $\text{LaAlO}_3$ ,<sup>9</sup> and  $\text{ZnGa}_2\text{O}_4$ ,<sup>10</sup>

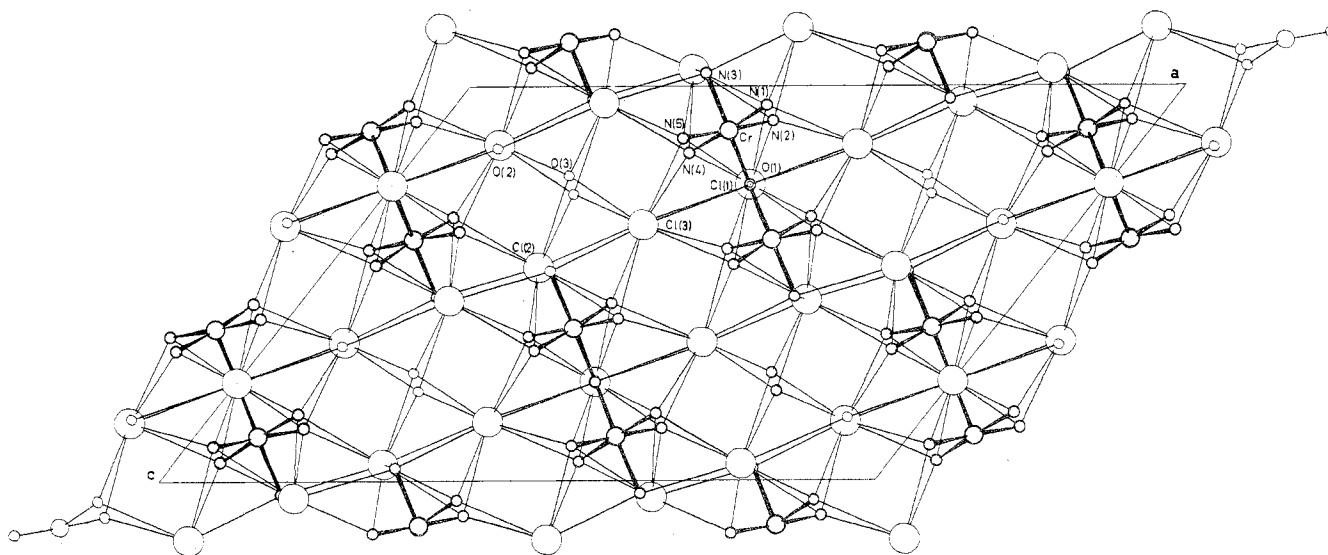
have been found to be due to this mechanism. Finally, there has been strong evidence for the existence of a vibronically induced exchange mechanism,<sup>11</sup> particularly in the absorption spectrum of the basic rhodo chromium(III) complex, where we have a linear Cr-O-Cr arrangement.

In order to create a basis for an analysis of the polarized absorption spectrum we decided to determine the crystal structure of acid rhodo chromium dihydrate. Crystals of this compound are most suitable for spectroscopic investigations. Various sets of spectra can be measured perpendicular to the well-developed faces of the crystal.

### Experimental Section

**Collection and Reduction of the X-Ray Data.** Acid rhodo chromium chloride was prepared by the method of Linhard and Weigel.<sup>12</sup> Crystals of the dihydrate were grown by slow evaporation of a saturated solution at 5 °C and pH 4. For the x-ray experiments a crystal had to be sealed into a capillary of Lindemann glass together with some mother liquor to prevent decomposition. The crystal was aligned with its  $b$  axis approximately parallel to the capillary tube. Weissenberg photographs showed that the crystals belong to the monoclinic system. The systematic absences observed on the diffraction pattern were  $h + k$  even for  $hkl$  and  $l$  even for  $h0l$ , which indicates that the space group is either  $Cc$  ( $C_2^4$ ) or  $C2/c$  ( $C_{2h}^6$ ). The intensity distribution<sup>13-16</sup> clearly suggests that the centrosymmetric space group  $C2/c$  is the more probable one. The following expectation values for various functions of the normalized structure factor  $E$  were obtained:  $\langle |E| \rangle = 0.806$ ,  $\langle |E|^2 \rangle = 1.009$ ,  $\langle ||E|^2 - 1| \rangle = 0.958$ . These indications are supported by the different distribution of vectors in the Patterson function for the two space groups.<sup>17</sup> The cell constant  $b$  was determined from an oscillation photograph along the  $b$  axis. The other cell constants were calculated by a least-squares procedure from eight reflections with  $\theta > 67^\circ$  measured on a zero-layer Weissenberg photograph calibrated with Si-powder lines. The wavelengths were assumed as  $\lambda(\text{Cu } K\alpha_1)$  1.540 51 Å and  $\lambda(\text{Cu } K\alpha_2)$  1.544 33 Å. The

\* To whom correspondence should be addressed at the Institut für anorganische Chemie, CH-3000 Berne 9, Switzerland.



**Figure 1.** Projection of the crystal structure of acid rhodo chromium chloride dihydrate parallel to the *b* axis. The  $N_5CrOCrN_5$  units are emphasized. The projection demonstrates that the twofold axes of the  $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$  complexes are parallel to the crystal *b* axis.

final lattice parameters are  $a = 23.656$  (9) Å,  $b = 7.36$  (1) Å,  $c = 16.718$  (8) Å,  $\beta = 128.1$  (1)°. The density of  $1.54 \text{ g cm}^{-3}$  calculated for four dimeric formula units in the cell is in good agreement with the observed value of  $1.55 \text{ g cm}^{-3}$  determined by the flotation method. Hence, the dimer is constrained to be on a fourfold position with symmetry  $C_2$ . The crystal specimen used to collect intensities had dimensions  $0.04 \times 0.02 \times 0.03 \text{ cm}$ . The intensities were recorded both with the film method and with a Supper Pace diffractometer using Mo  $K\alpha$  radiation and a graphite monochromator. Here we report only the diffractometer data. Layers could only be measured around the *b* axis, because the crystal was mounted in a capillary tube. A total of 1386 reflections out to a value of  $2\theta = 45^\circ$  were recorded at  $16^\circ\text{C}$ . The standard deviation was calculated according to

$$\sigma(I) = (P + m^2 B)^{1/2}$$

*B* is the background measurement for  $1/m$  of the time of the peak measurement *P*. A total of 274 reflections with  $I < 2.57\sigma(I)$  were assumed as unobserved. Lorentz-polarization corrections<sup>18</sup> were calculated but no absorption correction was applied. Because the crystal was mounted in a Lindemann tube, the application of an absorption correction would have been rather difficult.

**Solution of the Structure.** The structure was solved by direct methods.<sup>19,20</sup> Two phases were fixed to determine the origin and for another five reflections with high *E* values all possible phase combinations were calculated. Among the 32 combinations four had a low *Q* criterion

$$Q = \sum ||E_o| - |E_c|| / \sum |E_o|$$

with

$$|E_o| = |E_H| + |\sum E_K \cdot E_{H-K}| / \sum |E_K E_{H-K}|$$

Among these four the correct solution with  $Q = 0.03$  showed all atoms except the hydrogen atoms. The refinement was done with a block-diagonal least-squares routine,<sup>21</sup> the function minimized being  $\sum w(|F_o| - 1/k|F_c|)^2$ . The weighting scheme used was

$$w = 1/(8 + |F_o| + 0.01|F_c|^2)$$

The atomic scattering factors were taken from ref 22. After several cycles of refinement with isotropic temperature factors the agreement factor

$$R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

was 0.15. A difference Fourier synthesis showed that the positions of the two water molecules were not fully occupied, the occupancies being 0.7 and 0.8, respectively. With anisotropic temperature factors the structure refined to *R* values of 0.091 for the observed reflections

**Table I.** Positional Parameters for  $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5 \cdot 2H_2O$

Atom	<i>x</i>	<i>y</i>	<i>z</i>	Occupancy
Cr	0.41058 (7)	0.02555 (24)	0.11247 (10)	
O(1)	0.5000	0.0758 (17)	0.2500	
N(1)	0.4357 (5)	0.2217 (16)	0.0486 (6)	
N(2)	0.4626 (4)	-0.1680 (17)	0.0881 (6)	
N(3)	0.3147 (5)	-0.0206 (15)	-0.0332 (6)	
N(4)	0.3798 (4)	-0.1704 (16)	0.1692 (6)	
N(5)	0.3558 (4)	0.2176 (16)	0.1327 (6)	
H(1)	0.500	0.211	0.250	
Cl(1)	0.5000	0.4988 (7)	0.2500	
Cl(2)	0.2941 (1)	0.4673 (5)	0.4576 (2)	
Cl(3)	0.3940 (1)	0.1146 (5)	0.3512 (2)	
O(2)	0.1073 (7)	0.1016 (21)	0.1582 (10)	0.7
O(3)	0.2368 (5)	0.2995 (16)	0.2267 (7)	0.8

and 0.105 for all reflections. In the final cycle of least-squares calculation 1386 reflections were included and 104 parameters were refined. The greatest shift of any parameter was smaller than 0.3 its estimated standard deviation. The final difference Fourier showed a peak at the calculated position of the hydrogen atom on the bridging oxygen atom. No other hydrogen positions could be seen. All calculations were done with the crystallographic program system of the University of Berne.<sup>23</sup>

**Crystal Spectra.** Polarized single-crystal absorption spectra were measured on a Cary 17 spectrometer. Cooling was achieved by means of a helium gas flow technique. Three sets of spectra were recorded (cf. Figure 1): (A) light approximately parallel to *b* axis, *E* vector approximately parallel and perpendicular to *c*, respectively; (B) light approximately parallel to *c* axis, *E* vector parallel and perpendicular to *b* axis, respectively; (C) light perpendicular to *bc* plane, *E* parallel to *b* and *c*, respectively. Rectangular *bc* faces are well developed in most crystals.

## Results

**Description of the Structure.** A projection of the crystal structure is shown in Figure 1 and positional parameters are given in Table I. The  $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$  complexes are well separated from the  $Cl^-$  anions and the water molecules; no distance is shorter than 3.11 Å. The geometry of the cation is shown in Figure 2. The bridging oxygen lies on a crystallographic twofold axis, but the symmetry of the complex is almost  $C_{2v}$ . The coordination around the chromium atom is very close to that of a regular octahedron (Table II). The Cr-N distances range from 2.081 (9) to 2.091 (9) Å. The long bond length of 2.15 Å for the trans Cr-N (3) bond

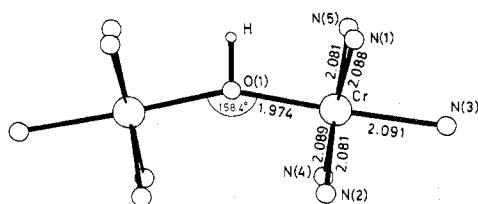


Figure 2. Projection of  $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]^{5+}$ .

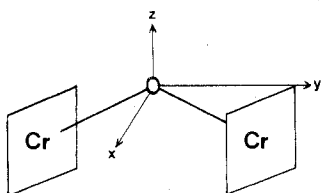


Figure 3. Coordinate system in dinuclear  $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]^{5+}$ .  $z$  is the twofold axis of the molecule,  $y$  lies in the plane defined by  $\text{CrOCr}$ , and  $x$  is perpendicular to this plane.

reported in the structure of the tetragonal rhodo chloride monohydrate by Hodgson et al.<sup>2</sup> could not be observed. The Cr-O bond length of 1.974 (5) Å is somewhat longer than the value of 1.94 (2) Å reported for the monohydrate. This can be explained by the smaller Cr-O-Cr angle of 158.4 (7)° compared with the value of 166° found by Hodgson et al.<sup>2</sup> The Cr-Cr separation is 3.878 (2) Å. The chloride ions together with one water molecule (O(2)) and two vertices of the octahedron (O(1), N(3)) form layers parallel (101) similar to the layers parallel (100) in the NaCl structure. Consecutive layers are separated by 4.27 Å and do not form a NaCl-type structure but are shifted by a vector  $[0, \frac{1}{2}, 0]$  with respect to the NaCl structure. The octahedron of the Cr complex and the second water molecule (O(3)) lie between these layers.

**Spectroscopic Results.** The knowledge of the crystal structure together with the polarized crystal spectra enables us to determine the polarizations of the various absorption bands with respect to the symmetry axes of the complex. In Figure 3 we define our coordinate system within the  $\text{N}_5\text{CrOCrN}_5$  framework. Figures 4-6 show three sets of polarized absorption spectra in the region between 14 400 and 17 000

Table II. Intermolecular Distances (Å) and Angles (deg) for  $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]^{5+}$

Distances			
Cr-O(1)	1.974 (3)	Cr-N(4)	2.089 (9)
Cr-N(1)	2.088 (9)	Cr-N(5)	2.081 (8)
Cr-N(2)	2.081 (9)	O(1)-H	0.99
Cr-N(3)	2.091 (8)		
Angles			
O(1)-Cr-N(1)	91.6 (3)	N(2)-Cr-N(3)	90.5 (3)
O(1)-Cr-N(2)	91.0 (3)	N(2)-Cr-N(4)	91.7 (4)
O(1)-Cr-N(4)	91.3 (3)	N(3)-Cr-N(4)	89.2 (3)
O(1)-Cr-N(5)	90.6 (3)	N(3)-Cr-N(5)	87.9 (3)
N(1)-Cr-N(2)	89.1 (4)	N(4)-Cr-N(5)	88.2 (3)
N(1)-Cr-N(3)	87.9 (3)	Cr-O(1)-Cr	158.4 (7)
N(1)-Cr-N(5)	90.9 (3)		

$\text{cm}^{-1}$ . The transitions observed in this spectral region correspond to  ${}^4\text{A}_{2g} \text{ } {}^4\text{A}_{2g} \rightarrow {}^4\text{A}_{2g} \text{ } {}^2\text{E}_g$ ,  ${}^4\text{A}_{2g} \text{ } {}^2\text{T}_{1g}$  single pair excitations. These transitions are known to be electric dipole. From the projection in Figure 1 it is seen that  $z$  coincides with the  $b$  axis, and  $x$  and  $y$  form angles of approximately 30 and 60°, respectively, with the  $c$  axis. From this the following relations are deduced

$$\begin{aligned} \text{crystal} & & \text{molecule} \\ \text{intensity } (E: \parallel b, \perp c) &= \text{intensity } (z) \\ \text{intensity } (E: \parallel c, \perp b) &= \frac{3}{4} [\text{intensity } (x)] + \frac{1}{4} [\text{intensity } (y)] \\ \text{intensity } (E: \perp c, \perp b) &= \frac{1}{4} [\text{intensity } (x)] + \frac{3}{4} [\text{intensity } (y)] \end{aligned}$$

Going back to the spectra in Figures 4-6 and using the above relations we see easily that some of the most prominent absorption bands are completely polarized either in the  $x$ ,  $y$ , or  $z$  direction, respectively. These bands are marked  $x$ ,  $y$ , and  $z$ , respectively, in Figures 4-6. The transitions observed in the 7-K spectrum, on the other hand, occur in more than one polarization.

The above results lead us to some conclusions concerning the intensity-gaining mechanisms involved in the pair absorptions. Transitions gaining their intensity solely through an exchange-induced mechanism are expected to be polarized purely along one of the symmetry axes of the polynuclear complex. We can therefore exclude a pure Tanabe mechanism as a source of intensity for most of the transitions observed in the 7-K spectra in Figures 4-6. These transitions are spin

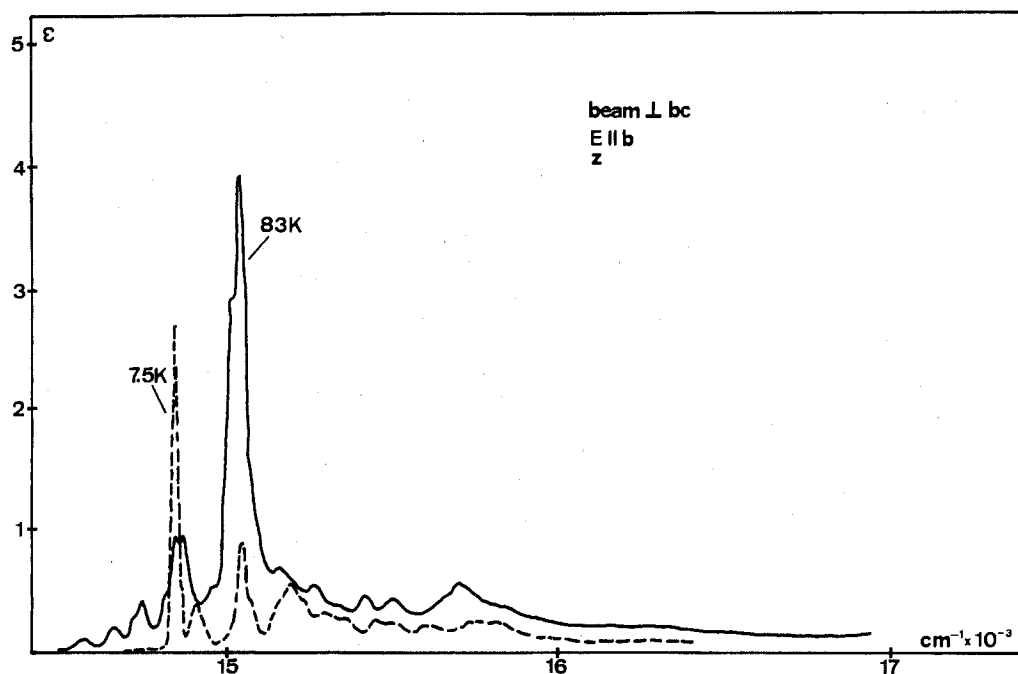


Figure 4. Single-crystal absorption spectrum of  $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]\text{Cl}_5 \cdot 2\text{H}_2\text{O}$ . The beam is perpendicular to the well-developed  $bc$  face of the crystal. The light is linearly polarized with the electric vector parallel to the  $b$  axis.

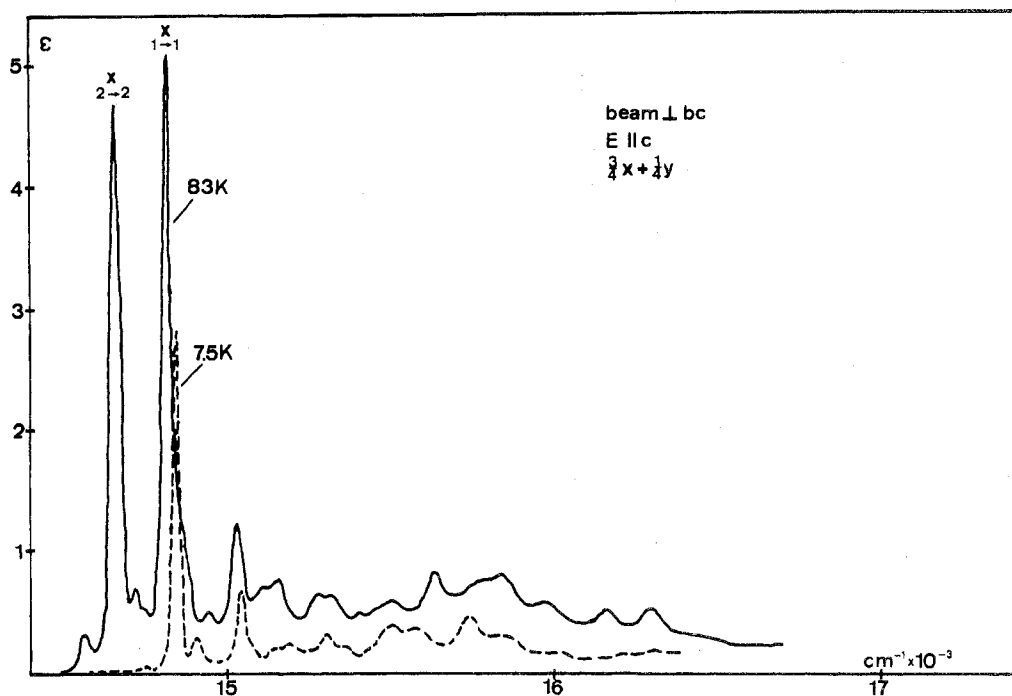


Figure 5. Same as Figure 4, but with polarization  $E \parallel c$ .

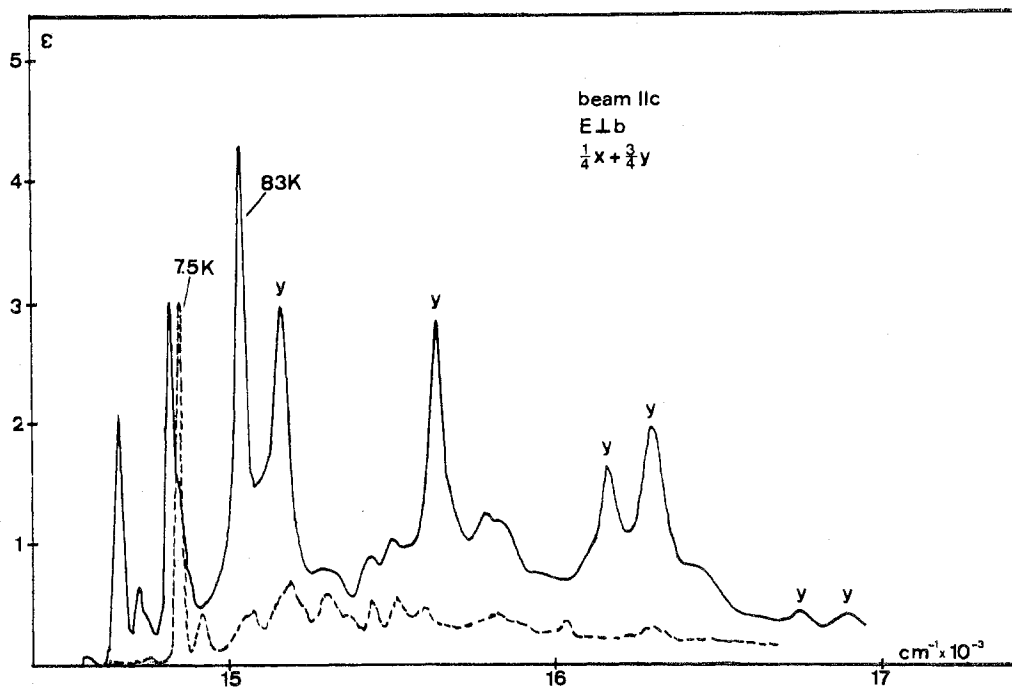


Figure 6. Same as Figure 4, but with the beam approximately parallel to the  $c$  axis and polarization  $E \perp b$ .

forbidden, a clear indication that spin-orbit coupling effects are important. If, on the other hand, we take the two prominent  $x$ -polarized bands at  $14652$  and  $14812 \text{ cm}^{-1}$  there is very strong evidence that they are purely exchange induced. Dubicki<sup>3</sup> has shown that selection rules based on the Tanabe mechanism predict their  $x$  polarization. Theory further predicts an intensity ratio for the two transitions  $2 \rightarrow 2$  ( $14652 \text{ cm}^{-1}$ ) and  $1 \rightarrow 1$  ( $14812 \text{ cm}^{-1}$ ) of<sup>8</sup>

$$\frac{[\overline{W}(3/2 \ 3/2 \ 1/2 \ 3/2; 21)]^2}{[W(3/2 \ 3/2 \ 1/2 \ 3/2; 11)]^2} = \frac{1.80}{1.0}$$

( $W$  = Racah  $W$  coefficient). This is in excellent agreement with the experimental ratio of 1.86 (corrected for Boltzmann

population). A further confirmation of the presence of an exchange mechanism in these two absorptions comes from a consideration of the various components contributing to the exchange-induced transition moment.

For spin-flip transitions the exchange-induced transition moment can be written as

$$\vec{P} = \sum_{i,j} \vec{\Pi}_{a_i b_j} (\vec{s}_{a_i} \cdot \vec{s}_{b_j}) \quad (1)$$

where  $i$  and  $j$  refer to electrons in orbitals  $\xi$ ,  $\eta$ , and  $\zeta$  on atoms  $a$  and  $b$ , respectively.<sup>8</sup> Using the above operator, it can be shown that the transition moments for the two  $x$ -polarized transitions which we are considering here involve the components  $\Pi_{\xi\xi}^x$  and  $\Pi_{\eta\eta}^x$ .<sup>9</sup> In a nearly linear Cr-O-Cr ar-

rangement  $\Pi_{\xi\xi}^x$  and  $\Pi_{\eta\eta}^x$  are expected to be the dominant terms because  $\xi_a(\eta_a)$  and  $\xi_b(\eta_b)$  can overlap with the same oxygen p orbital leading to a strong interaction.<sup>3</sup> This is in good agreement with the observed high intensities of the two bands at 14 652 and 14 812  $\text{cm}^{-1}$ .

We therefore conclude that the polarized absorption spectrum of the dinuclear chromium(III) complex  $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]^{5+}$  in the region of single pair excitations  ${}^4A_{2g}{}^4A_{2g} \rightarrow {}^4A_{2g}{}^2E_g$ ,  ${}^4A_{2g}{}^2T_{1g}$  offers clear evidence for the presence of at least two intensity-gaining mechanisms. The determination of the crystal structure was necessary to obtain this information.

**Acknowledgment.** Financial support by the Swiss National Science Foundation is gratefully acknowledged.

**Registry No.**  $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]\text{Cl}_5 \cdot 2\text{H}_2\text{O}$ , 62521-11-3.

**Supplementary Material Available:** Listings of structure factor amplitudes and anisotropic temperature factors (11 pages). Ordering information is given on any current masthead page.

## References and Notes

- (1) References in ref 2 and 4.
- (2) J. T. Veal, D. Y. Jeter, J. C. Hempel, R. P. Eckberg, W. E. Hatfield, and D. Hodgson, *Inorg. Chem.*, **12**, 2928 (1973).
- (3) L. Dubicki, *Aust. J. Chem.*, **25**, 739 (1972).
- (4) J. Ferguson and H. U. Güdel, *Aust. J. Chem.*, **26**, 505 (1973); J. Ferguson, H. U. Güdel, and M. Puza, *ibid.*, **26**, 513 (1973).

- (5) A. Urushiyama, T. Nomura, and M. Nakahara, *Bull. Chem. Soc. Jpn.*, **43**, 3971 (1970).
- (6) M. Naito, *J. Phys. Soc. Jpn.*, **34**, 1491 (1973).
- (7) J. Ferguson, private communication.
- (8) Y. Tanabe, T. Moriya, and S. Sugano, *Phys. Rev. Lett.*, **15**, 1023 (1965); J. Ferguson, H. J. Guggenheim, and Y. Tanabe, *J. Phys. Soc. Jpn.*, **21**, 692 (1966).
- (9) J. P. Van der Ziel, *Phys. Rev. B*, **4**, 288 (1971).
- (10) G. G. P. Van Gorkom, J. C. M. Henning, and R. P. Van Staple, *Phys. Rev. B*, **8**, 955 (1973).
- (11) H. U. Güdel and L. Dubicki, *Chem. Phys.*, **6**, 272 (1974); H. U. Güdel, *Chem. Phys. Lett.*, **36**, 328 (1975).
- (12) M. Linhard and M. Weigel, *Z. Anorg. Allg. Chem.*, **299**, 25 (1959).
- (13) E. R. Howells, R. C. Phillips, and D. Rogers, *Acta Crystallogr.*, **3**, 210 (1950).
- (14) J. Karle and H. Hauptman, *Acta Crystallogr.*, **6**, 131 (1953).
- (15) I. L. Karle, K. S. Dragonette, and S. A. Brenner, *Acta Crystallogr.*, **19**, 713 (1965).
- (16) G. N. Ramachandran and R. Srinivasan, *Acta Crystallogr.*, **13**, 429 (1959).
- (17) P. Engel and W. Nowacki, *Acta Crystallogr., Sect. B*, **24**, 77 (1968).
- (18) H. A. Levy and R. D. Ellison, *Acta Crystallogr.*, **13**, 270 (1960).
- (19) H. Hauptman, and J. Karle, "Solution of the Phase Problem. I. The Centrosymmetric Crystal", A.C.A. Monograph No. 3, Letter Shop, Wilmington, Del., 1953.
- (20) G. Germain and M. M. Woolfson, *Acta Crystallogr., Sect. B*, **24**, 91 (1968).
- (21) J. S. Rollet, "Computing Methods in Crystallography", Pergamon Press, Oxford, 1965.
- (22) K. Lonsdale, "International Tables for X-Ray Crystallography", Vol. III, Kynoch Press, Birmingham, England, 1962.
- (23) P. Engel, *Z. Kristallogr., Kristallgeom., Kristallphys., Kristallchem.*, **142**, 456 (1975).

Contribution from the Guelph-Waterloo Centre for Graduate Work in Chemistry, Waterloo Campus, Department of Chemistry, University of Waterloo, Waterloo, Ontario, Canada N2L 3G1

## Synthesis and Spectroscopic Characterization of Binuclear, Phosphido-Bridged $\sigma$ - $\pi$ -Acetylide Complexes of Iron. X-Ray Structure of a Triphenylphosphine Derivative

WAYNE F. SMITH, JOHN YULE, NICHOLAS J. TAYLOR, HANG N. PAIK, and ARTHUR J. CARTY\*

Received December 1, 1976

AIC60866N

The syntheses of a range of binuclear  $\sigma$ - $\pi$ -acetylide complexes of iron  $\text{Fe}_2(\text{CO})_6(\text{C}_2\text{R})(\text{PR}'\text{R}'')$  ( $\text{R} = \text{R}' = \text{R}'' = \text{Ph}$ ;  $\text{R} = \text{R}' = \text{Ph}$ ,  $\text{R}'' = \text{C}_2\text{Ph}$ ;  $\text{R} = \text{Ph}$ ,  $\text{R}' = \text{Bu}^t$ ,  $\text{R}'' = \text{C}_2\text{Ph}$ ;  $\text{R} = \text{Bu}^t$ ,  $\text{R}' = \text{R}'' = \text{Ph}$ ;  $\text{R} = \text{Pr}^i$ ,  $\text{R}' = \text{R}'' = \text{Ph}$ ;  $\text{R} = \text{Cy}$ ,  $\text{R}' = \text{R}'' = \text{Ph}$ ) from phosphinoacetylenes  $\text{RC}\equiv\text{CPR}'\text{R}''$  and diiron enneacarbonyl are described. These compounds and the corresponding  $\text{PPh}_3$  substitution products  $\text{Fe}_2(\text{CO})_5(\text{C}_2\text{R})(\text{PR}'\text{R}'')(\text{PPh}_3)$  have been characterized by microanalysis and infrared, mass, and Mössbauer spectroscopy. Single crystals of  $\text{Fe}_2(\text{CO})_5(\text{C}_2\text{Ph})(\text{PPh}_2)(\text{PPh}_3) \cdot \text{C}_6\text{H}_{12}$  are triclinic, space group  $P\bar{1}$ , with cell dimensions  $a = 17.975$  (8),  $b = 10.143$  (6),  $c = 13.181$  (8) Å;  $\alpha = 95.10$  (7),  $\beta = 112.30$  (4),  $\gamma = 97.54$  (4)°. There are two molecules in the unit cell. The structure was solved by a combination of Patterson and Fourier techniques using 3973 independent observed reflections ( $I > 3\sigma(I)$ ) measured on a GE-XRD6 diffractometer. Refinement by full-matrix least-squares methods gave values of  $R$  and  $R_w$  of 0.038 and 0.045, respectively. In the binuclear molecule the two iron atoms ( $\text{Fe}(1)$ - $\text{Fe}(2) = 2.648$  (1) Å) are bridged by a diphenylphosphido group and an acetylide  $\sigma$ -bonded to  $\text{Fe}(1)$  and  $\pi$ -bonded to  $\text{Fe}(2)$ . The  $\sigma$ - $\pi$ -acetylide has a C(6)-C(7) acetylenic bond length of 1.225 (6) Å and has a trans bent configuration. The triphenylphosphine molecule occupies a terminal position on  $\text{Fe}(1)$  ( $\text{Fe}(1)$ -P(2) = 2.274 (1) Å) trans to the phosphorus atom of the phosphido bridge. The mode of formation of these  $\sigma$ - $\pi$ -acetylides and structural similarities to  $\sigma$ - $\pi$ -vinyl complexes are discussed.

## Introduction

Recognition of the enhancement and modification of reactivity afforded by  $\pi$  coordination of acetylenes has led to the discovery of synthetic routes to numerous important organometallic and organic compounds.<sup>1-5</sup> For metals in low oxidation states, it is generally accepted that  $\pi$ -coordinated acetylenes are susceptible to electrophilic attack although mechanisms have been firmly established in relatively few cases.<sup>6</sup> Dimerization and oligomerization of acetylides by low-valent metal complexes are special cases.<sup>1-3</sup> Acetylene  $\pi$  complexes are accepted intermediates but the oligomerization may proceed via concerted multicentered or ionic mechanisms. Cyclobutadiene,<sup>7</sup> metallocyclic,<sup>8</sup> and  $\sigma$ -acetylide<sup>9</sup> complexes have been frequently postulated intermediaries.

During the course of studies designed to trap various  $\pi$ -acetylene intermediates using phosphinoacetylenes we investigated the reactions of  $\text{Fe}_2(\text{CO})_9$  and  $\text{Fe}_3(\text{CO})_{12}$  with ligands of the type  $\text{R}_2\text{PC}\equiv\text{CR}$ . A common feature of these reactions is the facile cleavage of a P-C<sub>sp</sub> bond which occurs in the formation of trinuclear ferracyclopentadiene<sup>10</sup> and ferracyclobutene<sup>11</sup> complexes from  $\text{Fe}_3(\text{CO})_{12}$  as well as  $\sigma$ - $\pi$ -acetylide<sup>12</sup> and phosphoniacyclopentadiene<sup>3</sup> complexes from  $\text{Fe}_2(\text{CO})_9$ . The possible role of acetylide complexes in these reactions and in other oligomerization sequences prompted a more detailed investigation of the synthesis, characterization, and reactions of  $\sigma$ - $\pi$ -acetylide complexes of type I. This paper describes a general route to these derivatives from  $\text{Fe}_2(\text{CO})_9$ . Since the initial characterization