lead to a lower symmetry of the crystal lattice. $MgCsPO_4\cdot 6H_2O$, $MgNH_4PO_4\cdot 6H_2O$, and $MgTlPO_4\cdot 6H_2O$ show smooth sharp ν_3 absorption bands with little or no splitting, and no ν_1 absorption band is observed. Tl^+ has an ionic radius close to that of NH_4^+ and therefore the compound would be expected to be similar to struvite. $MgCsPO_4\cdot 6H_2O$ has a new structure of high symmetry. From this it is concluded that the Cs, Tl, and NH_4^+ analogs have regular tetrahedral PO_4^{3-} groups; this agrees with the observation of Whitaker et al.[5,6] that the tetrahedral angles of PO_4^{3-} deviate less than 1° from ideal. The alkali ions in $MgKPO_4\cdot 6H_2O$ and $MgRbPO_4\cdot 6H_2O$ have ionic radii which are farther from NH_4^+ and both show splitting of the ν_3 absorption band. In $MgRbPO_4\cdot 6H_2O$ the splitting is severe and the ν_1 absorption band can be seen at 990 cm^{-1}. This indicates a lower symmetry for the Rb analog and possibly the K analog. This is consistent with the observation that these two are the least stable of the struvite analogs. Apparently K^+ and Rb^+ do not fit as well into the struvite structure as the larger ions. The Rb analog is transitional between the struvite structure and the $MgCsPO_4\cdot 6H_2O$ structure. This raises the possibility of phase transitions in $MgRbPO_4\cdot 6H_2O$.

In other respects the infrared spectra of the struvite analogs are remarkably similar. This might be expected as the spectra basically reflect the $(Mg(H_2O)_6PO_4)^-$ host lattice and the changes in the spectra are due to the interaction of the univalent ions with the PO_4^{3-} groups in this host lattice.

VI. Conclusions

The struvite structure shows a tendency to incorporate univalent ions ranging in size from 1.33 Å for K 1.69 Å for Cs. For K^+ (R = 1.33 Å), Tl^+ (R = 1.44 Å), NH_4^+ (R = 1.48 Å), and Rb^+ (R = 1.48 Å) the structure is orthorhombic. For the larger Cs^+ (R = 1.69 Å) ion, a hexagonal structure becomes stable. The Tl^+ analog appears to be the most stable and the NH_4^+ analog is also reasonably stable at room temperature, possibly due to hydrogen bonding. Both the K^+ and Rb^+ compounds decompose with time when removed from the mother liquor, indicating that the larger and smaller ions are somewhat strained in the orthorhombic structure. The hexagonal form of the Cs^+ analog also may transform to a cubic form at higher temperatures.

The struvite analogs offer a unique opportunity to study the effect of ionic size on a family of hydrated phosphates. The substitution of NH_4^+ into the struvite lattice containing K^+, Rb^+, and Tl^+ has been observed. Only one of these preparations was chemically analyzed; it has the approximate composition $MgTl_{1/3}(NH_4)_{2/3}PO_4\cdot 6H_2O$. Whether or not this composition is fortuitous is not known. A study of the system $MgM_xM'_{1-x}PO_4\cdot 6H_2O$ would yield valuable information about ordering, site preference, and the effect of ionic size on this structure. We do not know whether a reversible transition exists between hexagonal and cubic $MgCsPO_4\cdot 6H_2O$. We do know that at 40° only the hexagonal phase was observed and at higher temperatures mixtures of hexagonal and cubic phases were observed. However, the cubic phase was not seen without the presence of the hexagonal phase at room temperature. It seems possible that the strained orthorhombic $MgRbPO_4\cdot 6H_2O$ may exist in the hexagonal form at higher temperatures or with partial substitution of Cs^+ for Rb^+ ions.

Registry No. $MgNH_4PO_4\cdot 6H_2O$, 13478-16-5; $MgCsPO_4\cdot 6H_2O$, 54774-72-0; $MgKPO_4\cdot 6H_2O$, 19004-04-7; $MgRbPO_4\cdot 6H_2O$, 54774-73-1; $MgTlPO_4\cdot 6H_2O$, 54774-74-2; struvite, 15490-91-2.

References and Notes

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(2) (a) Abstracted in part from a dissertation submitted by R. Chianelli to the Department of Chemistry, Polytechnic Institute of New York, in partial fulfillment of the requirements for the Ph.D. degree, June 1974. (b) Abstracted in part from a thesis submitted by R. Korenstein to the Department of Chemistry, Polytechnic Institute of New York, in partial fulfillment of the requirements for the B.S. degree, June 1973.

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Single-Crystal Polarized Electronic Spectra of the Pentakis(2-picoline *N*-oxide)cobalt(II) Perchlorate Complex

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Single-crystal polarized electronic spectra of the pentakis(2-picoline *N*-oxide)cobalt(II) perchlorate complex, $[Co(C_6H_7NO)_5](ClO_4)_2$, have been recorded for a crystal modification, the structure of which has been determined. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions a = 10.223 (3) Å, b = 9.659 (3) Å, c = 38.195 (12) Å, β = 107.92 (3)°, and Z = 4. The structure was refined to an R factor of 0.076. Assignment of the transitions on the basis of a C_{2v} symmetry is proposed and the energies of the electronic levels are discussed in terms of ligand field and angular overlap parameters.

Introduction

In the framework of a research program based on single-crystal spectra tending to test the validity of ligand field models for low-symmetry chromophores[1-3] it seemed interesting to investigate the pentakis(2-picoline *N*-oxide)cobalt(II) perchlorate complex[4] (CoO_5) which is reported to be approximately trigonal bipyramidal.[5] The fact that the donor atoms are five oxygens belonging to five equal ligands should simplify the problem of interpreting the spectra and should therefore give more information on the ligand ability of pyridine

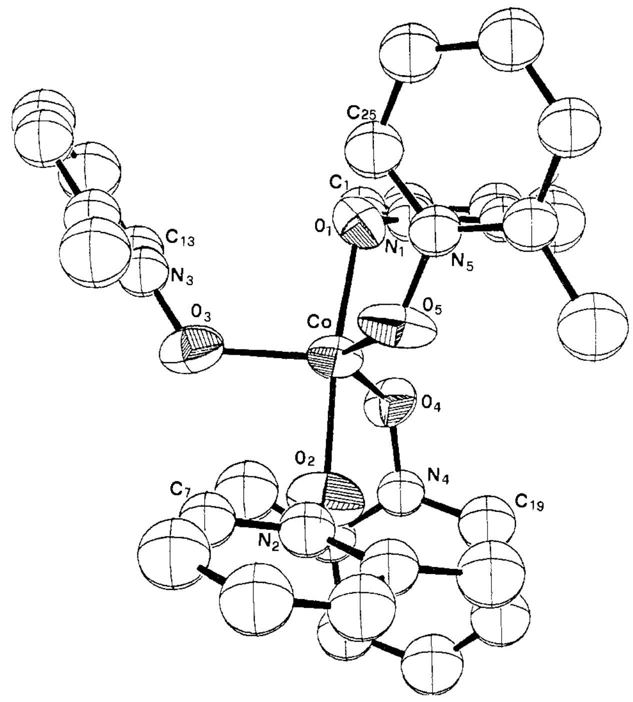

Figure 1. A perspective view of the $Co(C_6H_7NO)_5{}^{2+}$ cation (ORTEP diagram). The numbering of the picoline carbon atoms increases starting from the numbered carbon atom.

N-oxide type of ligands.

Experimental Section

According to the X-ray report the $[Co(C_6H_7NO)_5](ClO_4)_2$ crystallizes in two crystal modifications which appear as needles and prisms, respectively. The structure had been solved only for the latter form.[5] However, we were able to grow large crystals only of the needle form and therefore had to solve again the X-ray structure.

Collection of X-Ray Data. The $[Co(C_6H_7NO)_5](ClO_4)_2$ crystals having needle shape are monoclinic, space group $P2_1/c$, with a = 10.223 (3) Å, b = 9.659 (3) Å, c = 38.195 (12) Å, β = 107.92 (3)°, V = 3588.5 Å^3, d_{measd} = 1.48 g cm^{-3}, Z = 4, mol wt 803.47, and d_{calcd} = 1.491 g cm^{-3}. Cell parameters were determined by least-squares refinement of 20 2θ values. Data were collected on a four-circle Philips automatic diffractometer, using a θ–ω scan technique. The crystal used for data collection had dimensions 0.6 × 0.25 × 0.03 mm. Scans of 0.7° in ω in 10 sec were executed across the peaks, and background was counted for 5 sec on each side of the peaks. The radiation used was Mo Kα monochromatized with a flat graphite crystal. The standard deviations on the intensities were calculated with the expression $\sigma = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (0.02I)^2]^{1/2}$,[6] where P is the peak count, B_1 and B_2 are the background counts, T_p and T_b are the count times on the peak and the background, respectively, and I is the intensity. The 1620 reflections, of a total of 3737 collected in the range $6 \leq 2\theta \leq 40°$, having $I \geq 3\sigma(I)$ were considered observed reflections and were used in the structure analysis. The Lorentz–polarization correction was applied to the observed reflections. An absorption correction was applied using the Tompa analytical method;[7] the transmission factors were in the range 0.86–0.98. Scattering factors were taken from ref 8 for neutral cobalt, chlorine, oxygen, nitrogen, and carbon atoms and from ref 9 for hydrogen atoms.

Solution and Refinement of the Structure. The positions of the cobalt and chlorine atoms were obtained from a three-dimensional Patterson synthesis. Two three-dimensional Fourier syntheses showed the positions of all nonhydrogen atoms of the structure. Refinement was performed with the full-matrix least-squares program of Busing and Levy, adapted by Stewart.[10] The minimized function was $\sum w(|F_o| - |F_c|)^2$, where w is the weight assigned to the F_o values, according to the expression $w = 1/\sigma^2{}_{F_o}$. Anisotropic temperature factors were used for cobalt, chlorine, and oxygen atoms, and isotropic factors, for nitrogen and carbon atoms. The hydrogen atoms were introduced in calculated positions (C–H = 0.9 Å) with an overall B temperature factor of 5 Å^2 and were not refined.

At the end of the refinement the R factor was 0.076, and the R factor, defined as $\sum[w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, was 0.084. The oxygen atoms of the two perchlorate ions converged to very high thermal parameters and a ΔF Fourier synthesis calculated at the end of refinement gave some indications of disorder for these atoms: the greatest peak of this synthesis had a height of about 1 e Å^{-3} and is in proximity to the Cl(2) atom.

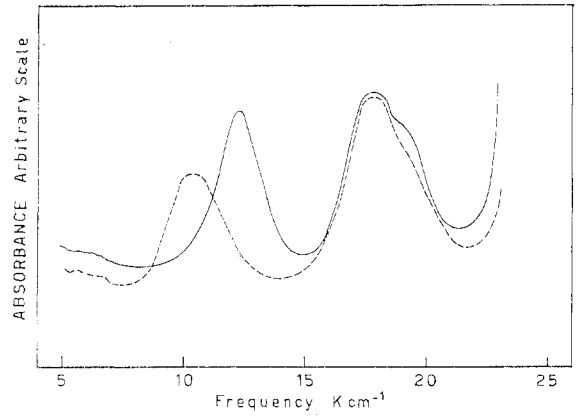

Figure 2. Single-crystal spectra of the CoO_5 chromophore: - - -, spectrum recorded along c^*; ——, spectrum recorded along b.

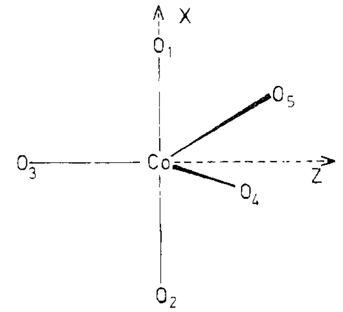

Figure 3. A sketch of the $Co(C_6H_7NO)_5{}^{2+}$ cation with the chosen molecular axes.

Spectrophotometric Measurements. Single-crystal polarized electronic spectra were measured on a SP 700 Unicam spectrophotometer modified as described elsewhere.[11]

Results and Discussion

Description of the Structure. The structure consists of discrete $Co(C_6H_7NO)_5{}^{2+}$ and ClO_4^- ions. The cobalt atom is pentacoordinate, linked to the five oxygen atoms of the 2-picoline *N*-oxide molecules. The coordination polyhedron geometry can be described as a distorted trigonal bipyramid (Figure 1). The positional parameters of the atoms are reported in Tables I and II and selected distances and angles are in Table III. The geometry of the chromophore does not differ substantially from that found by Coyle and Ibers[5] on the other crystal modification of the same complex. Indeed, the distortions with respect to an idealized trigonal-bipyramidal geometry are of the same kind and of the same amount for both crystal structures. For example the O(1)–Co–O(2) angle is 172.5 (4)° in our case and 173.4 (4)° in Ibers' case and the equatorial angles are respectively 117.7 (4), 110.4 (4), and 131.5 (4)° vs. 115.4 (5), 113.7 (8), and 129.8 (8)°.

Single-Crystal Spectra. The needle-shaped crystals permitted recording the spectra along the b and c^* directions of the (101) face. These spectra show (see Figure 2) a band at 10.5 kK neatly c^* polarized, another band at 12.5 kK clearly b polarized, and a broad absorption centered at 18 kK which changes only in some details in the two polarizations. If we assume the molecular axes shown in Figure 3, the b spectrum is completely y polarized and the c^* spectrum is almost completely z polarized. If the symmetry felt by the metal ion were axial, the z and y spectra would have been identical whereas they are not. Therefore a symmetry lower than axial

Table I. Positional Parameters ($\times 10^4$), Anisotropic Temperature Factors[a] ($\times 10^3$), and Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Co	1073 (2)	4233 (2)	3654 (1)	40 (1)	35 (1)	59 (1)	−1 (1)	16 (1)	−4 (1)
Cl(1)	3910 (5)	41 (5)	2911 (1)	100 (4)	58 (3)	94 (4)	11 (3)	46 (3)	4 (3)
Cl(2)	2749 (4)	2929 (5)	200 (1)	84 (3)	80 (3)	87 (4)	−4 (3)	34 (3)	−3 (3)
O(1)	3188 (8)	4572 (8)	3751 (2)	45 (6)	43 (6)	62 (7)	−1 (5)	10 (5)	−7 (5)
O(2)	−921 (8)	3704 (9)	3611 (3)	55 (6)	42 (7)	117 (9)	3 (5)	30 (6)	−2 (6)
O(3)	539 (9)	4506 (9)	3112 (2)	64 (7)	57 (7)	72 (7)	1 (6)	25 (6)	4 (6)
O(4)	1610 (8)	2348 (9)	3846 (2)	61 (6)	45 (6)	60 (7)	9 (5)	17 (5)	16 (6)
O(5)	766 (8)	5960 (9)	3900 (3)	44 (6)	56 (7)	108 (8)	−8 (5)	33 (6)	−28 (7)
O(11)[b]	4633 (17)	1284 (16)	2969 (4)	258 (18)	117 (13)	231 (17)	−64 (13)	177 (15)	−70 (12)
O(12)	2557 (16)	397 (16)	2703 (4)	205 (15)	185 (16)	176 (14)	59 (12)	66 (12)	42 (13)
O(13)	4376 (13)	−863 (12)	2682 (4)	173 (12)	82 (9)	190 (13)	−20 (9)	130 (10)	−35 (10)
O(14)	3767 (16)	−557 (15)	3214 (4)	253 (16)	114 (14)	108 (11)	45 (13)	104 (11)	49 (11)
O(21)	3529 (12)	3465 (13)	−1 (4)	138 (11)	137 (11)	155 (13)	−8 (9)	102 (10)	48 (10)
O(22)	1903 (17)	1794 (17)	46 (4)	234 (17)	165 (17)	194 (16)	−70 (13)	128 (14)	−51 (13)
O(23)	1698 (18)	3977 (20)	115 (5)	202 (17)	198 (20)	199 (17)	9 (15)	89 (14)	5 (15)
O(24)	3233 (17)	3123 (18)	575 (4)	227 (16)	234 (18)	110 (13)	−71 (14)	17 (12)	49 (13)

[a] Anisotropic thermal factors are of the form $\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* \cos\gamma^* + 2U_{13}hla^*c^* \cos\beta^* + 2U_{23}klb^*c^* \cos\alpha^*)]$. [b] Oxygen atoms of the perchlorate ions.

Table II. Positional Parameters ($\times 10^4$), Isotropic Temperature Factors ($\times 10^3$), and Estimated Standard Deviations in Parentheses

Atom	*x*	*y*	*z*	*U*, Å^2
N(1)	4096 (9)	3638 (10)	3943 (3)	42 (3)
N(2)	−1899 (10)	4665 (11)	3563 (3)	53 (3)
N(3)	1381 (9)	4961 (11)	2937 (3)	47 (3)
N(4)	630 (10)	1421 (11)	3877 (3)	47 (3)
N(5)	1650 (10)	6982 (10)	4042 (3)	46 (3)
C(1)	4597 (14)	2739 (15)	3747 (4)	59 (4)
C(2)	5539 (15)	1749 (16)	3936 (5)	67 (5)
C(3)	5911 (15)	1672 (16)	4302 (5)	72 (5)
C(4)	5395 (15)	2618 (16)	4494 (4)	67 (5)
C(5)	4449 (12)	3582 (14)	4305 (3)	44 (4)
C(6)	3837 (15)	4638 (17)	4481 (4)	88 (6)
C(7)	−2363 (14)	5233 (14)	3232 (4)	58 (4)
C(8)	−3407 (16)	6169 (17)	3147 (4)	84 (5)
C(9)	−3944 (15)	6545 (17)	3439 (5)	85 (5)
C(10)	−3465 (14)	6004 (15)	3768 (4)	69 (5)
C(11)	−2349 (13)	4981 (15)	3846 (4)	56 (4)
C(12)	−1789 (15)	4286 (18)	4190 (4)	91 (5)
C(13)	2300 (14)	4075 (16)	2863 (4)	61 (4)
C(14)	3180 (15)	4444 (17)	2675 (4)	75 (5)
C(15)	3071 (16)	5717 (20)	2546 (4)	86 (5)
C(16)	2151 (16)	6623 (16)	2605 (4)	72 (5)
C(17)	1284 (14)	6232 (15)	2783 (4)	62 (4)
C(18)	136 (15)	7135 (17)	2843 (4)	86 (5)
C(19)	454 (14)	1362 (15)	4209 (4)	65 (5)
C(20)	−524 (16)	440 (17)	4245 (4)	75 (5)
C(21)	−1203 (15)	−336 (17)	3964 (4)	83 (5)
C(22)	−1026 (15)	−281 (16)	3634 (4)	76 (5)
C(23)	−3 (13)	677 (15)	3586 (4)	60 (4)
C(24)	317 (16)	801 (18)	3246 (5)	98 (5)
C(25)	2409 (14)	7516 (15)	3842 (4)	62 (5)
C(26)	3275 (14)	8592 (16)	3983 (4)	64 (5)
C(27)	3340 (14)	9150 (16)	4319 (4)	69 (5)
C(28)	2568 (14)	8579 (15)	4503 (4)	63 (4)
C(29)	1711 (13)	7493 (15)	4369 (4)	51 (4)
C(30)	751 (16)	6889 (16)	4561 (4)	85 (5)

Table III. Distances and Angles in the Coordination Group with Their Estimated Standard Deviations

		Distance, Å			
Co-O(1)	2.104	0.008	Co-O(4)	1.977	0.008
Co-O(2)	2.058	0.009	Co-O(5)	1.987	0.010
Co-O(4)	1.989	0.009			
		Angle, Deg			
O(1)-Co-O(2)	172.5	0.4	O(2)-Co-O(4)	87.5	0.4
O(1)-Co-O(3)	95.8	0.4	O(2)-Co-O(5)	87.1	0.4
O(1)-Co-O(4)	85.7	0.3	O(3)-Co-O(4)	117.7	0.4
O(1)-Co-O(5)	95.1	0.3	O(3)-Co-O(5)	110.4	0.4
O(2)-Co-O(3)	90.1	0.4	O(4)-Co-O(5)	131.5	0.4

Table IV. Observed and Calculated Spectral Band Energies for the CoO_5 Chromophore[a]

Assignment	Freq, kK	
	Obsd	Calcd in C_{2v} symmetry
$^4B_2$-$^4B_1$	⩽5	5.0
$^4B_2$	10.5	10.6
$^4A_1$	12.5	12.4
$^4B_1$		18.2
$^4B_2$	18.0	18.2
$^4A_2$		18.7

[a] Parameter values: $Dq_{eq} = 1.05$ kK; $I_2/I_4 = 0.55$; $Dq_{ax}/Dq_{eq} = 0.9$; $\alpha = 115°$; $\beta = 0.85$.

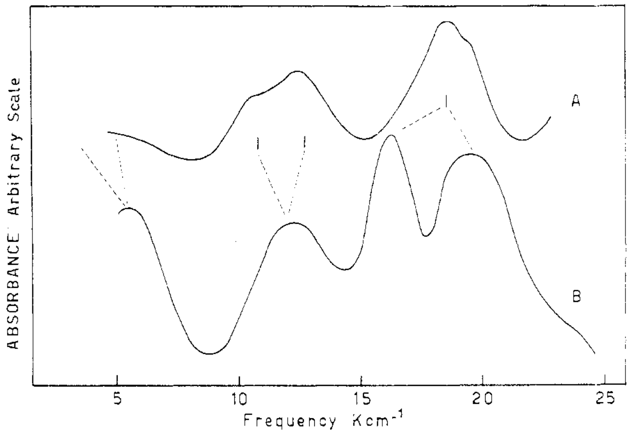

Figure 4. Diffuse-reflectance spectra of the CoO_5 (A) and CoN_4Br (B) chromophores.

must be assumed. By inspecting the chromophore one realizes that a C_{2v} symmetry with the C_2 axis parallel to *z* is quite close to the actual arrangement of the donor atoms. Along the lines of this assumption the polarization properties are accounted for by assigning, as shown in Table IV, the band at 10.5 kK to the *z*-allowed B_2–B_2 transition and the band at 12.5 kK to the *y*-allowed B_2–A_1 transition. The absorption at 18 kK is assigned to the three F–P transitions. Two of them are expected to be *x* and *z* polarized and one is not allowed. The fact that this band does not show any neat polarization can be ascribed to the proximity of the three excited levels which presumably are mixed also with the levels arising from doublet terms. Indeed, when the F–P transitions are quite close in energy to each other, no neat polarizations are often observed.[12-14] Finally both the solution and the reflectance spectra show at ≃5 kK the tail of a weak band which can be tentatively assigned to the unallowed B_2–B_1 transition, although a tail of a lower lying allowed transition could also be present.

Comparison between the Spectra of CoO_5 and CoN_4Br Chromophores. In Figure 4 the reflectance spectra of the CoO_5 and bromotris(2-dimethylaminoethyl)aminecobalt(II) bromide

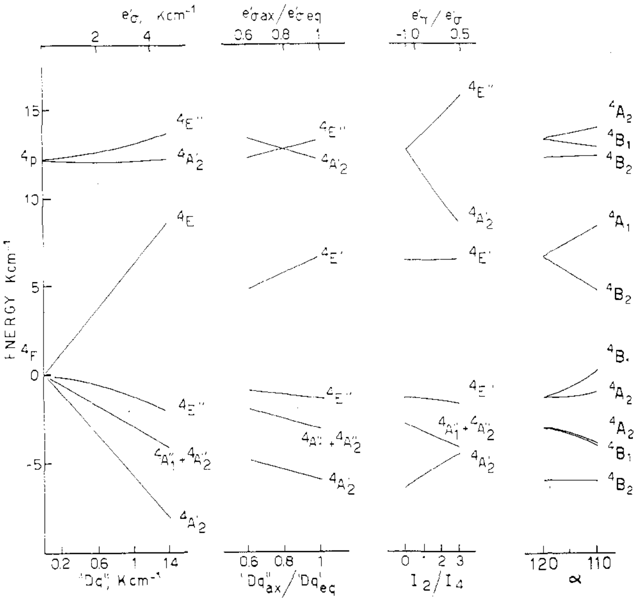

Figure 5. Energy level diagrams for a cobalt(II) ion in D_{3h} symmetry as functions of crystal field and angular overlap parameters (see eq 1 and 2): $Dq_{ax}/Dq_{eq} = 1, I_2/I_4 = 0.55, \beta = 0.85$. From the left to the right the effect of changing the Dq_{ax}/Dq_{eq} ratio and the I_2/I_4 ratio, as well as the effect of a C_{2v} distortion toward a square pyramid, is shown.

(CoN_4Br)[15] complexes are shown with their assignments. The latter complex is also trigonal bipyramidal with donor set N_4Br.[16] Its spectra were assigned on the basis of C_{3v} symmetry.[3,17] The main spectral differences between the two chromophores are (1) the F–P transitions are well split in the CoN_4Br complex but not in the CoO_5 complex and (2) the bands of the CoO_5 chromophore are at lower energies. The latter observation can be accounted for by the lower field strength of oxygen with respect to nitrogen.[18] The former observation can be rationalized only by inspecting the ligand field diagrams reported in Figure 5. The F–P transitions become closer when the radial integral ratio, I_2/I_4, decreases or when Dq_{ax}/Dq_{eq}[19] decreases. Now, the apical Co–O distances are ca. 2.1 Å whereas the equatorial Co–O distances are ca. 1.97 Å. Therefore, the spectral pattern is well accounted for by the structural data. Finally it should be noted that by a first inspection of the two spectra of Figure 4 one could be tempted to relate the band at 16 kK of the CoN_4Br complex with that at 12.5 kK of the CoO_5 derivative. Actually the polarized spectra definitely show that the bands at 10.5 and 12.5 kK of CoO_5 are due to the splitting of an E level of C_{3v} symmetry which for the CoN_4Br complex falls at 12 kK.

Attempts for a Quantitative Assignment. From the ligand field diagrams reported in Figure 5 it appears that the F–P transitions are close to each other when $Dq_{ax}/Dq_{eq} < 1$ and/or I_2/I_4 is small (<1.5). Moreover, the large value of the F–P transitions indicates a relatively small nephelauxetic effect, as previously observed in pyridine *N*-oxide ligands.[20] The splitting of the transitions to the highest E(F) levels markedly depends upon the C_{2v} distortion. The energy level diagrams for a C_{2v} chromophore are shown in Figure 6. The separation between the two highest A_1(F) and B_2(F) levels does not depend significantly on the Dq_{ax}/Dq_{eq} ratio nor on the I_2/I_4 ratio. Therefore, given the large number of parameters and the actual C_1 symmetry of the molecule, it is possible to propose only a range for each of the ligand field parameters which give reasonable fittings. Such values are $Dq = 1.05$ kK, $Dq_{ax}/Dq_{eq} = 0.8–0.9$, $I_2/I_4 = 0.1$, and $\beta = 0.85$. These values are quite reasonable within the framework of a ligand field model. An indicative fitting is reported in Table IV.

Figures 5 and 6 show also the dependence of the energy levels on the e_σ' and e_π' parameters, as defined by Schäffer,[21] of the angular overlap model. These results have been obtained independently from an angular overlap calculation although it is now well established[19,21] that the I_2 and I_4 ligand field parameters are related to the angular overlap parameters according to eq 1 and 2. The e_σ' and e_π' parameters are related to the antibonding σ and π effects on the d metal orbitals if the donor atoms are imagined to be linearly ligating. The values of these parameters are proportional to the squares of the metal orbital–ligand orbital overlaps. The ratio of the squares of the overlaps for axial and equatorial oxygens was calculated to be 0.8 using Clementi's functions[22] for the cobalt d orbitals and oxygen p orbitals. This value compares quite well with the Dq_{ax}/Dq_{eq} values which match the spectra.

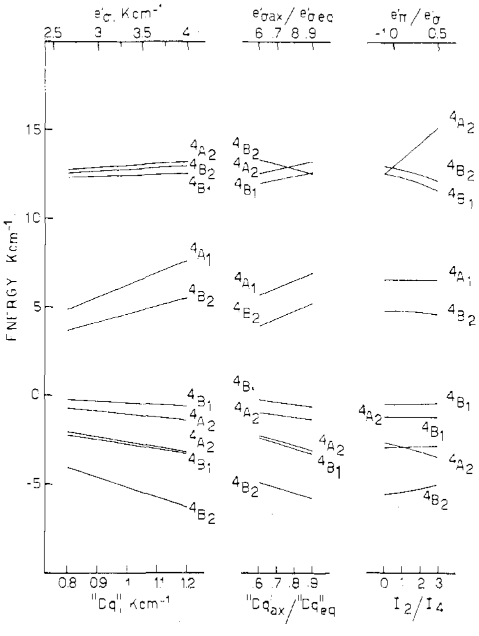

Figure 6. Energy level diagrams for a cobalt(II) ion in C_{2v} symmetry as functions of crystal field and angular overlap parameters (see eq 1 and 2): $Dq_{ax}/Dq_{eq} = 0.8, I_2/I_4 = 0.55, \beta = 0.85, \alpha = 115°$. The angle α and the axial and equatorial position are defined as in Figure 5. From the left to the right the effect of changing the Dq_{ax}/Dq_{eq} ratio and the I_2/I_4 ratio is shown.

$$Dq = I_4/6 = (3e_\sigma' - 4e_\pi')/10 \qquad (1)$$

$$I_2/I_4 = \frac{5e_\sigma'}{e_\pi'} + 5/(9e_\sigma'/e_\pi' - 12) \qquad (2)$$

The procedure of calculating independently some angular overlap parameters or at least a relation among them is a meaningful check of the validity of ligand field calculations.[19,21,23] However, when the I_2/I_4 values range between 0 and 1, it is difficult to have information on the relative importance of σ and π contributions to the coordinative bond. In fact, it follows from eq 2 that, for $0 < I_2/I_4 < 1$, e_σ'/e_π' is either smaller than -1 or larger than 4. The possibility of metal–oxygen back-bonding (e_σ'/e_π' negative) is improbable on the basis of contact shift investigations.[20,24,25] Therefore π bonding in pyridine *N*-oxide complexes, if any, is of the donor to metal type.[25]

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Registry No. $[Co(C_6H_7NO)_5](ClO_4)_2$, 21460-56-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24×

reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th Street, N.W., Washington, D.C. 20036. Remit check or money order for $4.50 for photocopy or $2.50 for microfiche, referring to code number AIC403455.

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Synthesis, Characterization, and X-Ray Structure of Confacial-Bioctahedral Iron(II)- and Cobalt(II)-Hydrido Complexes with Tridentate Tripod Ligands Containing Phosphorus and Arsenic as the Donor Atoms

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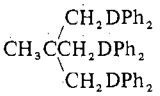
The dimeric hydrido complexes of iron(II) and cobalt(II) having the formula $[M_2H_3L_2]X$, where L is 1,1,1-tris(diphenylphosphinomethyl)ethane (p3) or 1,1,1-tris(diphenylarsinomethyl)ethane (as3) and X is PF_6 or BPh_4, have been prepared and characterized. The iron complexes are diamagnetic whereas the cobalt complexes have a magnetic moment corresponding to two unpaired electrons per molecule. The structures of the complexes $[Fe_2H_3(p_3)_2]PF_6\cdot1.5CH_2Cl_2$ and $[Co_2H_3(as_3)_2]BPh_4$ were determined by X-ray analyses using diffractometer data. Both cations have the structure $[LMH_3ML]^+$ (L = p3, as3; M = Fe, Co) with confacial-bioctahedral geometry. The shared face of the two octahedrons consists of three hydrogen atoms which bridge the gap between the two metal atoms. Each metal is bound to the three phosphorus or arsenic atoms of the ligand. The short Fe–Fe [2.332 (3) Å] and Co–Co [2.377 (8) Å] distances suggest that multiple metal–metal bonds may be present.

Introduction

The tripod ligands 1,1,1-tris(diphenylphosphinomethyl)ethane (p3) and 1,1,1-tris(diphenylarsinomethyl)ethane (as3)



$$CH_3C(CH_2DPh_2)_3$$

p_3: D = P
as_3: D = As

(the latter first synthetized in this laboratory) have been used to prepare complexes with 3d metals in oxidation states from 0 to +2.[1-11] The ligand p3 has been found to function as bidentate or tridentate, and complexes with iron, cobalt, and nickel have been described, the metal having four-, five-, or six-coordinate stereochemistry.

The p3 ligand reacts with cobalt(II) or nickel(II) halides in the presence of $NaBH_4$ to form the monovalent complexes $M(p_3)X$ (X = Cl or Br).[9] The $M(p_3)I$ complexes are obtained simply by the reaction of p3 with the nickel(II) and cobalt(II) iodides. Possibly the reducing agent is the ligand p3 which may form an iodide of pentavalent phosphorus. An X-ray structural analysis of $Ni(p_3)I$ derivative has shown this complex to have a distorted tetrahedral geometry.[12] The related four-coordinated complexes $Ni(as_3)X$ (X = Br or I) have also been previously described.[10]

When iron(II) or cobalt(II) salts react with p3 in the presence of $NaBH_4$ and bulky anions such as BPh_4^- or PF_6^-, hydrides of the formula $[M_2H_3(p_3)_2]Y$ (M = Fe, Co; Y = BPh_4, PF_6), containing the metal in the formal oxidation state +2, are obtained. With the ligand as3 only the cobalt(II) hydride $[Co_2H_3(as_3)_2]BPh_4$ could be prepared.

The complexes have been characterized by their electronic, infrared, and nmr spectra and by magnetic measurements. Complete X-ray structural analyses have been carried out for the compounds $[Fe_2H_3(p_3)_2]PF_6\cdot1.5CH_2Cl_2$ and $[Co_2H_3(as_3)_2]BPh_4$.

A preliminary account of part of this work has already been published.[13]

Results and Discussion of the Chemistry

When a solution of p3 and an iron salt (halides, tetrafluoroborate, perchlorate) in methylene chloride–alcohol, at room temperature, is allowed to react with sodium tetrahydroborate, an intense blue coloration is obtained. Upon addition of $NaBPh_4$ [or $((n\text{-}Bu)_4N)PF_6$] dark blue crystals of the composition $[Fe_2H_3(p_3)_2]Y\cdot x$(solvent) are precipitated. If the same reaction is carried out with the corresponding cobalt(II) halides, the monovalent metal complexes $Co(p_3)X$ are formed.[9] However when cobalt(II) salts of poorly coordinating anions, such as BF_4^-, are used and the reaction is carried out in alcohol–ethyl ether (or alcohol–tetrahydrofuran) at 0°, a cherry red solution is obtained from which the dark red complex $[Co_2H_3(p_3)_2]BPh_4\cdot x$(solvent) may be precipitated.