at the stoichiometric ratio of 6:1 at 0° or at an 8:1 ratio at the higher temperature of 25° always left unreacted $(CF_3)_2S_2$, since the formation of CF_3SF_5 uses excess AgF_2. At −15° only a very slight reaction had occurred after 18 hr and at −30° no reaction was detectable by infrared analysis after 116 hr.

Good yields of CF_3SFO were obtained by simply storing 1–2-g quantities of the product mixture in a 1-l. glass bulb for a few days until all of the CF_3SF_3 was converted to CF_3SFO and SiF_4. The CF_3SFO was purified by pumping off the CF_3SF_5 and SiF_4 at −111° (or more rapidly at −97°; however, some CF_3SFO also distils) followed by a distillation from a −86° trap which retains most of any residual $(CF_3)_2S_2$.

Analysis.—The CF_3SFO was identified by its molecular weight (calcd, 136; found, 137, by vapor density method), ^{19}F nmr spectrum (resonances in a 3:1 intensity ratio for CF_3 and SF at 84 and 26 ppm *vs.* external $CFCl_3$ at −50°), and mass spectrum (intensities were: CF_3^+, 100; SFO^+, 45; SO^+, 38; SF^+, 11; CF_2^+, 10; CF^+, 8; S^+, 6; CF_2S^+, 2; CF_3SO^+, 1; CF_3S^+, 0.6; CF_3SFO^+, 0.03 at 70 V). The infrared spectrum (Figure 1) has very strong bands at 1269 ($S \rightarrow O$ stretch), 1226 and 1151 (C–F stretch), and 752 cm^{-1} (S–F stretch, but probably coincident with a medium intensity C–S stretching band[6–8]), and it has medium intensity bands at 588, 481, and 412 cm^{-1}.

The CF_3SF_5 was identified by its infrared[9] and nmr[10] spectra. The CF_3SF_3 was identified by its ^{19}F nmr spectrum (CF_3 at 71 and SF_3 (exchange broadened[11]) at −30 ppm *vs.* $CFCl_3$ in an approximately 1:1 ratio), its reactivity with glass and moisture to give CF_3SFO, and its relative volatility.[3,4] No attempt was made to obtain a high-purity infrared sample, but the following bands of CF_3SF_3 were evident: 1242 vs and 1140 db, vs (C–F stretch), 850 s and 708 vs (S–F stretch),[12,13] 598 m and 517 m cm^{-1}. Other bands appear to be at 1265 and 750[6] cm^{-1} (where CF_3SFO impurities interfere) and at 560 w and 405–393 db cm^{-1}.

Infrared analysis was performed on a Beckman IR-12 spectrometer using a metal-valved Kel-F cell equipped with AgCl windows. Nuclear magnetic resonance studies were performed on a Varian Associates Model HA-100 spectrometer using Pyrex tubes. Mass spectral analysis was performed by Morgan-Schaeffer Corp., Montreal, Canada.

Reactions.—The hydrolysis of CF_3SFO by water vapor appears to give several products, depending on the conditions. Of particular interest is the observation of one or more compounds of low volatility characterized by carbonyl stretching frequencies in the 1740-cm^{-1} region and the C–H band around 2975 cm^{-1}. Other bands associated with this material were at 1370 ($S \rightarrow O$?), 1218 (PQR), and 532 (PQR) cm^{-1}. Hydrolysis in an infrared cell (Kel-F body, AgCl windows) left a nonvolatile material which apparently contained sulfonyl or sulfonate groups.

No reactions of CF_3SFO were observed when it was heated with activated[14–17] CsF (3 mmoles each in a 75-ml cylinder) for 4 hr at 120° and 16 hr at 135° or when held with AsF_5 (9.3 mmoles each in a Kel-F tube) for 48 hr at −78°. By comparison, SF_2O (unlike SF_4O[16,17]) also did not appear to react with CsF, but does react[15] with AsF_5 at −78° to give a solid complex (which is, however, completely dissociated at 25°, unlike the stable[18] complexes $SF_3^+AsF_6^-$ and $SF_3O^+AsF_6^-$). The CF_3SFO thus appears to be a poor or very weak fluoride acceptor or donor.

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[6] The conflicting assignments to C–S stretch and CF_3 deformation of medium intensity bands in the 750-cm^{-1} region for several CF_3S compounds have been reviewed.[7] The C–S bands in CH_3SO_2F, CH_3SO_2Cl, and $(CH_3)_2SO_2$ have been recently assigned[8] in this region, *i.e.*, outside the normal 600–700-cm^{-1} region for alkylsulfur compounds.

[7] J. K. Brown and K. J. Morgan, *Advan. Fluorine Chem.*, **4**, 303 (1965).

[8] M. Spoliti, S. M. Chackalackal, and F. E. Stafford, *J. Am. Chem. Soc.*, **89**, 1092 (1967).

[9] D. F. Eggers, Jr., and H. E. Wright, *J. Chem. Phys.*, **35**, 1045 (1961).

[10] C. I. Merrill, S. M. Williamson, G. H. Cady, and D. F. Eggers, *Inorg. Chem.*, **1**, 215 (1962).

[11] The SF_2 and SF resonances of CF_3SF_3 have been resolved by 100 ppm at lower temperatures by E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *ibid.*, **3**, 1298 (1964). The temperature dependence is analogous to that in F_4.

[12] The location of the S–F bands in CF_3SF_3 and $C_6H_5SF_3$[2] (807 cm^{-1}) suggests strongly that the compound reported as SF_3CF_2COOH[13] (which had an S–F band at 894 cm^{-1} and was remarkably stable to hydrolysis) is actually a pentafluorsulfur derivative (perhaps SF_5CH_2COOH).

[13] R. N. Haszeldine and F. Nyman, *J. Chem. Soc.*, 2684 (1956).

[14] Activation of cesium fluoride by vacuum drying a finely powdered sample at 150–170° for 2 hr, followed by a second regrinding in a drybox, has proved[15] quite satisfactory for the reaction[16,17] with SF_4O to give $Cs^+SF_5O^-$.

[15] E. W. Lawless, unpublished results.

[16] W. C. Smith and V. A. Engelhardt, *J. Am. Chem. Soc.*, **82**, 3939 (1960).

[17] J. K. Ruff and M. Lustig, *Inorg. Chem.*, **3**, 1422 (1962).

[18] F. Seel and O. Detmer, *Z. Anorg. Allgem. Chem.*, **301**, 8 (1959).

Contribution from the Department of Chemistry,
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An Analysis of the Ligand Field Spectrum of Pentacyanocobaltate(II)

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Increased interest in pentacoordination[2a] coupled with the interpretation[2b] of the esr spectrum of $Co(CN)_5^{3-}$ in terms of C_{4v} symmetry prompts us to communicate an analysis of the d-to-d spectrum of pentacyanocobaltate(II). All results have been obtained by diagonalizing the d^7 ligand field matrices[3] in the strong field basis for a field of C_{4v} symmetry.

Figure 1 depicts the splitting of the low-lying electronic states of O_h symmetry (far left) by the axial ligand field characteristic of a square-pyramidal structure. The negative values of the axial parameters *Ds* and *Dt* correspond to a weaker ligand field along the unique axis than in the equatorial plane due to the removal of an axial CN^- ligand. In this situation the ground-state electron configuration is $(e)^4(b_2)^2(a_1)^1(b_1)^0 = {}^2A_1$ as demanded by the observed *g* values.[4] Calculated and observed spectra are compared in Table I, and an assignment is given in terms of *approximate* one-electron transitions. In fitting the observed spectrum, the ratio C/B was fixed at the free ion value,[5] and a typical reduction in the Racah parameter *B* was introduced on the basis of the nephelauxetic effect.[6] Neglecting configuration interaction, the transition ${}^2A_1 \rightarrow {}^2A_2$ at 31.7 kK is independent of *Ds* and *Dt* at an energy $\Delta + 2B - C$. Having calculated an approximate Δ value in this way, the remaining three observed transitions fix the two parameters *Ds* and *Dt* within rather narrow limits. The figure shows that two additional states

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[1] National Science Foundation Graduate Fellow, 1965–1967.

[2] (a) E. L. Muetterties and R. A. Schunn, *Quart. Rev.* (London), **20**, 245 (1966); (b) J. J. Alexander and H. B. Gray, *J. Am. Chem. Soc.*, **89**, 3356 (1967). Professor Gray has subsequently measured the absorption spectrum at several temperatures in order to rule out the possibility of any structural equilibrium. Thus, all observed bands are now known to be due to a C_{4v} anion.

[3] R. Krishnamurthy, W. B. Schaap, and J. R. Perumareddi, *Inorg. Chem.*, **6**, 1338 (1967); J. R. Perumareddi, *J. Phys. Chem.*, **71**, 3144 (1967).

[4] The observed *g* values are incompatible with a ${}^2B_1$ ground state.

[5] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 766 (1954).

[6] C. K. Jørgensen, *Advan. Chem. Phys.*, **5**, 33 (1963).

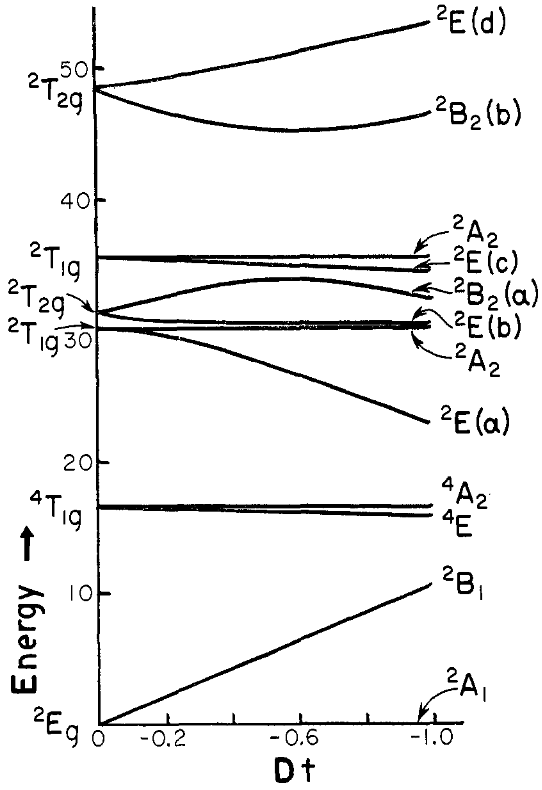

Figure 1.—Low-lying energy levels of a d^7 electronic configuration in a ligand field of C_{4v} symmetry. The $^2A_1$ state is fixed as the zero of energy. All energies are expressed in units of kilokaysers (1 kK = 1000 cm^{-1}). $Dq = 3.3$, $B = 0.75$, $Ds = 1.5Dt$, $C/B = 4.633$.

appear as a result of the departure of the complex from octahedral symmetry. As a result, bands appear at 10.35 and 23.30 kK in addition to the 16.2- and 31.7-kK bands which are approximately unaffected by axial distortions. While the 10.35-kK band is simply the $z^2 \rightarrow x^2 - y^2$ transition between the resolved components of the ^2E_g ground state of octahedral symmetry, the 23.30-kK band is strongly perturbed from octahedral symmetry. Since the lowest $^2T_{2g}$ and $^2T_{1g}$ excited states both give rise to ^2E states in a square-pyramidal ligand field and since the parent states are separated by only 0.85 kK, configuration interaction is strong between these states, and $^2E(a)$ falls rapidly. Consequently, although the transition is largely (86%) $e \rightarrow a_1$, a significant contribution (8%) comes from $e \rightarrow b_1$. In the same manner, the curvature of $^2B_2(a)$ is the result of repulsion by $^2B_2(b)$.

The assignments in Table I agree with those of Alexander and Gray[2b] with the exception of the band at 23.3 kK which we assign as $^2A_1 \rightarrow {}^2E(a)$. Since these authors based their assignment on a one-electron picture, they could not have anticipated the stronger configuration interaction within the ^2E states than that within the $^2B_2$ states which causes the $^2A_1 \rightarrow {}^2E(a)$ transition to appear at lower energies.

The value of $\Delta \equiv 10Dq = 33$ kK for pentacyanocobaltate(II), which is fixed by the transition energy to $^2A_2$ and $^2E(b)$, is very large and quite close to the Δ value[7] (34.8 kK) for $Co(CN)_6^{3-}$. The hexacyanides of Fe^{2+} and Fe^{3+}, with Δ values of 33.8 and 35 kK, respectively,[7] also show a striking lack of dependence of Δ on metal oxidation state. Thus, while Δ values for π-donor ligands increase about 10 kK upon changing the metal oxidation state from +2 to +3, the lack of dependence of Δ on metal oxidation state for π-acceptor ligands is apparently a rather general phenomenon.[8]

TABLE I

ELECTRONIC SPECTRUM OF PENTACYANOCOBALTATE(II)[a]

Obsd $\nu^{b,c}$	Calcd ν^{b}	Transition	Approximate one-electron description
10.35	10.19	$^2A_1 \longrightarrow {}^2B_1$	$a_1(z^2) \longrightarrow b_1(x^2 - y^2)$
16.20	15.93	$\longrightarrow {}^4E$	$b_2(xy) \longrightarrow b_1(x^2 - y^2)$
	16.52	$\longrightarrow {}^4A_2$	$e(xz,yz) \longrightarrow b_1(x^2 - y^2)$
23.30	23.42	$\longrightarrow {}^2E(a)$	$e(xz,yz) \longrightarrow a_1(z^2)$
31.70	30.34	$\longrightarrow {}^2A_2$	$b_2(xy) \longrightarrow b_1(x^2 - y^2)$
	30.41	$\longrightarrow {}^2E(b)$	$e(xz,yz) \longrightarrow b_1(x^2 - y^2)$

[a] $B = 0.75$, $Dq = 3.3$, $Dt = -0.95$, $Ds = -1.43$, all in units of kilokaysers; $C/B = 4.633$. [b] All energies in units of kilokaysers, 1 kK = 1000 cm^{-1}. [c] See ref 2b.

It has been emphasized recently that the degree of aggregation (solid, liquid, gas) may influence the geometry assumed by a molecule.[2a] In view of the fact that crystal-packing forces rather than intramolecular electronic factors seem to dictate the solid-state structure of pentacyanonickelate(II),[9] information on the geometry of the analogous pentacyanocobaltate(II) *in solution* is essential to any correlation of electronic structure with stereochemistry. The value of Dt compatible with the spectrum of $Co(CN)_5^{3-}$ gives some insight into the structure of this ion in solution. The crystal field formalism gives the following relation between Dq and Dt for a square pyramid of five cyanide ligands with equatorial–axial C–Co–C angle θ

$$Dt = -\frac{2}{7}\left[1 + 15\cos^2\theta - \frac{35}{2}\cos^4\theta\right]Dq(\mathrm{CN}^-) + \frac{2}{7}Dq(\mathrm{solvent})$$

Here, Dq(solvent) represents any field which might be imposed on the metal by a solvent molecule approaching the metal from below along the fourfold axis. The suggestion[10] that pentacyanocobaltate is actually a substituted octahedral complex with a normal bonding cobalt–oxygen distance can be tested by substituting $\theta = 90°$ and the Dq value for $Co(H_2O)_6^{2+}$ into the above equation. The resulting $Dt = -0.68$ kK is far enough from the Dt value derived from the observed spectrum to discount a substituted octahedral geometry.[11] Although this structure can be eliminated with confidence, this line of reasoning does not allow one to distinguish the presence or absence of weak solvation along the fourfold axis. Thus, no solvation (*i.e.*, Dq(solvent) = 0) and $\theta = 90°$ is as compatible with the Dt value of Table I as is an angle of about 95° in conjunction with a

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[7] H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, **85**, 2922 (1963).

[8] On the basis of this conclusion it is likely that Δ for $V(CO)_6^-$ may be equal to, or only slightly less than, Δ for $Cr(CO)_6$, owing to decreased stabilization of the t_{2g} orbital by the ligand π^* orbital in the latter compound.

[9] *Chem. Eng. News*, **44**, 43 (Nov 21, 1966).

[10] W. P. Griffith and G. Wilkinson, *J. Chem. Soc.*, 2757 (1959).

[11] Crystal field relations between Dt and Dq have been shown[3] to be accurate to at least 10%. See also R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, **4**, 709 (1965).

small *Dq*(solvent) value corresponding to weak solvation. In any event, the strong θ dependence of the angular function relating *Dq* to *Dt* makes angles of greater than approximately 98° highly unlikely.

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Structure and Properties of an Unusual Mixed Cobalt(III)–Cobalt(II) Diamine Chloro Complex Salt

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The preparation of a compound assumed to be *trans*-dichlorobis(N-methylethylenediamine)cobalt(III) chloride has been described by Basolo.[1] The only analytical result reported was a chloride determination, which had to be rationalized on the basis of a formulation containing HCl of crystallization, *viz.*, $Co(Meen)_2Cl_2 \cdot Cl \cdot 0.1HCl$ (Meen = $NHCH_3CH_2CH_2NH_2$). A recent reinvestigation in our laboratory of some of the properties of this compound has led to the conclusion that it is not simply a dichlorocobalt(III) complex. It is instead a mixed cobalt(III)–cobalt(II) complex of empirical formula $Co_3(Meen)_4Cl_8$. It contains dichlorobis(N-methylethylenediamine)cobalt(III) cations and tetrachlorocobaltate(II) anions in a ratio of 2:1.

Experimental Section

The preparative procedure duplicated that of Basolo[1] with minor modifications. Occluded HCl was removed from the crude material by dissolution in methanol and precipitation by addition of ethyl ether. The HCl-free complex was dried[2] for 2 days at 72°. Cobalt analyses were performed by the thermal decomposition of the complex as described by Charlot and Bezier,[3] nitrogen by the Dumas method,[4] and carbon and hydrogen by standard microchemical procedure.[5] The chloride analyses, done by conductometric titration using a General Radio Type 1650A impedance bridge in conjunction with bright platinum electrodes, were of two types: (1) immediate titration with aqueous silver nitrate of a freshly prepared aqueous solution of the complex ("exterior ionic chloride"); (2) back titration by chloride of excess silver nitrate remaining after boiling the aqueous complex solution containing the silver salt for 30 min. (This "total chloride" determination was confirmed by weighing the silver chloride precipitated in the boiling treatment just described.)

The infrared spectrum over the range 250–4000 cm^{-1} was obtained with a Perkin-Elmer Model 521 grating spectrophotometer utilizing solid complex and the KBr pellet technique. Spectra of aqueous and methanolic solutions of the complex were run on a Perkin-Elmer Model 202 spectrophotometer over the range 200–750 mμ. The solid reflectance spectrum of the complex diluted with lithium fluoride *vs.* a lithium fluoride standard was obtained with a suitably modified Beckman DU spectrophotometer. The proton magnetic resonance spectrum of a 10% solution of the complex in D_2O was recorded on a Varian A60 instrument using tetramethylsilane as a reference. Magnetic susceptibility measurements were made with a Varian water-cooled electromagnet (Model V4004) connected with a Model V2301A current regulator and a Model V2300A power supply. The field was standardized using $CuSO_4 \cdot 5H_2O$.

Results and Discussion

The analytical data are presented in Table I. It is to be noted that the observed total composition figures agree closely with calculations based on the trinuclear empirical formula already mentioned.

TABLE I

	Co	N	C	H	Cl[a]	Cl[b]
% calcd[c]	23.4	14.80	19.03	5.28	37.5	18.8
% obsd	23.5	14.81	18.96	5.75	37.5	18.8

[a] "Total chloride." [b] "Exterior ionic chloride." [c] On the basis of the formula $Co_3(Meen)_4Cl_8$.

The infrared spectrum has bands characteristic of the coordinated diamine and two strong bands attributed to a cobalt–chloride stretch at 275 and 295 cm^{-1}.[6–8] Upon replacement of the tetrahedrally bound and part of the octahedrally bound chloride by reaction of the complex with silver carbonate, the band at 295 cm^{-1} disappears, but the band at 275 cm^{-1}, apparently due to the more firmly bonded octahedrally coordinated Cl, remains.

The visible reflectance spectrum of the solid has a number of bands between 600 and 700 mμ, characteristic of $CoCl_4^{2-}$ as reported by Katzin,[9] which are not obtained from an aqueous or methanolic solution of the complex. The visible solution spectrum of the complex from 350 to 700 mμ is that normally associated with a *trans*-$Co(en)_2Cl_2^+$ type of cation. However, the addition of large amounts of LiCl or $(CH_3)_4NCl$ to methanolic solutions reestablishes the missing bands in the 600–700-mμ region. From this observation one concludes that the complex ion $CoCl_4^{2-}$ is present in the solid state, but hydrolyzes rapidly in dilute aqueous solution as expected. The "exterior chloride" data support this concept completely.

The observation that the complex is soluble only in polar solvents supports the conclusion that it is a salt in the solid state. The pH of a 0.1 *M* aqueous solution of the complex is about 4, thus indicating about 10^{-3}

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[1] F. Basolo, *J. Am. Chem. Soc.*, **75**, 227 (1953).

[2] Preparations at temperatures above 80° resulted in partial decomposition of the complex with the formation of more cobalt(II) species. Drying at temperatures up to 120° resulted in no detectable decomposition; however, decomposition resulted at about 135°.

[3] G. Charlot and D. Bezier, "Quantitative Inorganic Analysis," translated by R. C. Murray, John Wiley and Sons, Inc., New York, N. Y., 1957, p 408.

[4] Courtesy of the Testing and Inspection Spectral Laboratory of the National Aniline Division of Allied Chemical Corp., Buffalo, N. Y.

[5] Performed by Weiler and Strauss Microanalytical Laboratory, Oxford England.

[6] D. M. Adams, J. Chatt, J. M. Davidson, and J. Gerratt, *J. Chem. Soc.*, 2189 (1963).

[7] A. Sabatini and L. Sacconi, *J. Am. Chem. Soc.*, **86**, 17 (1964).

[8] G. W. Watt and D. S. Klett, *Inorg. Chem.*, **3**, 782 (1964).

[9] L. I. Katzin, *J. Am. Chem. Soc.*, **76**, 3089 (1954).