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Magnetic Investigations of Spin-free Cobaltous Complexes. III. On the Existence of Planar Complexes

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Magnetic and spectral data are presented for 14 spin-free complexes of Co(II) which are either quadricoördinate or which have a tetragonally distorted octahedral coördination shell; in all cases but one all donor atoms are oxygen. It is concluded that the quadricoördinate complexes are planar. Planar, spin-free, quadricoördinate complexes of Co(II) have not heretofore been generally recognized.

In Parts I and II[1,2] of this series we have discussed in detail the magnetic properties of a diverse group of tetrahedral cobaltous complexes and have demonstrated how, using a model based on ligand field theory, the relative magnitudes of the orbital contributions to the magnetic moments of these complexes can be interpreted. In Part II were developed some empirical structure-magnetism correlations which we now wish to apply to a body of magnetic data in order to present strong evidence for the existence of a hitherto unrecognized class of Co(II) complexes, *viz.*, those which are quadricoordinate, planar and spin-free (three unpaired electrons).

There is actually very little direct evidence in the form of X-ray structural determinations for the existence of planar quadricoördinate Co(II) complexes of either the spin-free or spin-paired type. There is no evidence of any sort on the spin-free complexes and the only spin-paired complex which has been examined is bis-(salicylal)ethylenediimine Co(II) which is planar.[3] However, phthalocyanine and porphyrin complexes of Co(II) are undoubtedly planar since this stereochemistry is imposed by the ligand. These complexes together with numerous others whose magnetic data have been summarized by Figgis and Nyholm[4] all have one unpaired electron and orbital contributions equal to or less than approximately 1 B.M. and may reasonably be assumed to be planar.

TABLE I

MAGNETIC DATA FOR Co(II) ACETYLACETONATE

	T (°K.)	$\chi_{corr}^{m} 10^{-6\,a}$	μ_{eff} (B.M.)[b]
Solid	296.7	10,150	4.93 ($\theta = 0°$)
	194.9	14,930	5.02 ($\theta = -13°$)
	74.2	35,500	
Solution[b]			
Pyridine	300.8	9,573	4.82
Benzene	301.4	9,497	4.81
Chloroform	300.6	9,406	4.77
Methanol	302.7	10,060	4.96

[a] Diamagnetic correction for acetylacetonate chelate rings were derived from the measured diamagnetic susceptibility of Zn acetylacetonate for which $\chi^{m} = -123 \pm 6 \times 10^{-6}$. [b] Calcd. from $\mu_{eff} = 2.84 (\chi_{corr}^{m} T)^{1/2}$.

In this work a series of quadricoördinate cobaltous complexes has been studied and the magnetic data are given in Tables I and II. All of these complexes except one are of the Co–O_4 type, *i.e.*, the cobalt is coördinated only by oxygen. The hydrates with at least $2H_2O/Co$ are quite likely not strictly quadricoördinate (*vide infra*). The prototype of this series is bis-(acetylacetonato)-Co(II), CoA_2. This compound and three others in the series have been synthesized previously and their magnetic moments reported. The previously reported moments of CoA_2, 4.2,[5,6] 4.32[7] and 3.9[8]

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(1) R. H. Holm and F. A. Cotton, *J. Chem. Phys.*, **31**, 788 (1959).

(2) R. H. Holm and F. A. Cotton, *ibid.*, in press.

(3) E. D. Hughes, C. Barkelew and M. Calvin, quoted in Martell and Calvin, "Chemistry of Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952, p. 266.

(4) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 12 (1954).

(5) D. P. Mellor and R. J. Goldacre, *J. Proc. Roy. Soc. N. S. Wales*, **73**, 233 (1940).

(6) E. Feytis, *Compt. rend.*, **152**, 708 (1911).

(7) L. Cambi and S. Szego, *Ber.*, **64**, 2591 (1931).

TABLE II

MAGNETIC DATA FOR COMPLEXES OF THE TYPE $Co-O_4$

Compound	T (°K.)	$\chi_{corr.}^{m} 10^{-6}$	Diamagnetic corr.	μ_{eff} (θ = 0°)
Bis-(acetylacetonato)-Co(II)·$2H_2O$	302.6	10,300	−151	5.02
Bis-(benzoylacetonato)-Co(II)	296.4	10,120	−199	4.92
Bis-(benzoylethylacetato)-Co(II)	297.3	9,996	−174	4.90
Bis-(benzoylethylacetato)-Co(II)·$2H_2O$	293.7	10,180	−200	4.91
Bis-(trifluoroacetylacetonato)-Co(II)	294.8	10,380	−155	4.97
in benzene	296.6	9,984	−155	4.89
Bis-(trifluoroacetylacetonato)-(Co(II)·$^5/_2H_2O$	294.4	10,180	−187	4.92
Bis-(hexafluoroacetylacetonato)-Co(II)·$^5/_2H_2O$	296.2	9,932	−199[a]	4.87
Bis-(salicylaldehyde)-Co(II)	299.6	9,608	−161	4.82
Bis-(salicylaldehyde)-Co(II)·$2H_2O$	299.8	9,301	−187	4.74[d]
Bis-(tropolonato)-Co(II)	298.3	9,741	−152[c]	4.84
Co(II) kojate·$^1/_2H_2O$	297.0	9,720	−142[b]	4.83[f]
Co(II) guaiacolate	299.0	10,540	−144	5.04[e]
Bis-(S-ethylthioglycolato)-Co(II)[g]	298.6	10,000	−137	4.91
Bis-(formylcamphor)-Co(II)·$2H_2O$				5.05[h]
Sodium bis-(*o*-phthalato)-cobaltate(II)·H_2O				5.35 (ref. 5)
Bis-(3-hydroxypyrone)-Co(II)				5.17[i]

[a] $\chi^m(CF_3COCH_2COCF_3$·hydrate$) = -83 \pm 5 \times 10^{-6}$. [b] χ^m(kojic acid) $= -68 \pm 4 \times 10^{-6}$. [c] $\chi^m(C_7H_6O_2) = -70 \pm 4 \times 10^{-6}$. [d] Reported 4.5, ref. 18. [e] Reported 4.5, ref. 20. [f] Reported 4.8, ref. 22. [g] Of the type $Co-O_2S_2$. [h] D. P. Mellor, *J. Proc. Roy. Soc. N. S. Wales*, **75**, 157 (1942). [i] L. Sacconi, *Gazz. chim. ital.*, **80**, 372 (1950).

had been interpreted in the framework of valence bond theory as indicative of a tetrahedral sp^3 structure with an orbital contribution due to the three unpaired electrons in the non-bonding d orbitals of the metal. The moment of CoA_2 obtained here for the solid, measured over a temperature range, and for solutions is significantly higher than the earlier values. Indeed, remeasurement of moments for those $Co-O_4$ complexes already reported plus measurements on new complexes of the same general type reveal that in all cases the magnetic moment is greater than 4.8 B.M. These orbital contributions of approximately 0.9–1.1 B.M. cannot be said to be inconsistent with the valence bond formulation of the tetrahedral structure nor can they be said to support it because the planar outer-orbital dsp^2 structure is equally consistent. It will now be argued in terms of ligand field theory that the size of the orbital contribution in $Co-O_4$ complexes is too large to be compatible equally with both the planar and tetrahedral conformations and, indeed, militates strongly against the latter.

Consider the position of oxygen-bearing ligands in the following spectrochemical series[2]: $I^- < Br^- < Cl^- < OH^- < NO_3^- < F^- < C_2O_4^{2-} \lesssim H_2O <$ py $\lesssim NCS^- < NH_3 <$ en $\gtrsim NO_2^- <$ *o*-phen $\lesssim$ dip $<< CN^-$. It has been shown previously[1,2] that orbital contributions in tetrahedral Co(II) complexes decrease as the ligands vary from I^- toward CN^-, *i.e.*, as the intensity of the ligand field increases. On the basis of existing data[2] it is expected that a "normal" tetrahedral $Co-O_4$ arrangement, such as in the hypothetical tetrahedral ion $Co(OH_2)_4^{+2}$, would provide a magnetic moment in the approximate range 4.5–4.7 B.M. and exhibit a strong absorption band ($\epsilon = 10^2–10^3$) with a λ_{max} in the 600–700 mμ range.[1,9,10] No obvious steric factors or large differences in the electronic natures of the donor oxygens which could produce an abnormally weak or strong ligand field are evident in these complexes[11a] so that significant deviations from these approximate ranges are not anticipated. In all cases the moments of the quadricoördinate $Co-O_4$ complexes are greater than those for the known cases of $Co-O_4$ tetrahedra,[2,11b] *viz.*, $Co[(p\text{-}Me_2NC_6H_4)_3PO]_4(ClO_4)_2$ (4.76 B.M.), $Co(Ph_3PO)_4(ClO_4)_2$ (4.72 B.M.), $Co(Me_3PO)_4(ClO_4)_2$ (4.34 B.M.) and Co^{+2} in ZnO-(4.26 B.M.). Furthermore, the moments reported here exceed that for $CoCl_4^{-2}$ (4.80 B.M.) and many are larger than that for $CoBr_4^{-2}$ (4.87 B.M.). It has been concluded in Part II that moments for tetrahedral complexes of the type CoL_4 where L is not a halide could not exceed 4.80 ± 0.05 B.M. because no ligand is known to occur between Cl^- and I^- in the spectrochemical series except Br^-. In fact, several reported moments (Table II) exceed that for CoI_4^{-2}, 5.01 ± 0.05 B.M., which is a definite upper limit for any tetrahedral Co(II) complex regardless of its ligands because no ligand is known to produce a weaker field than iodide. Comparison of moments from Parts I and II and from Table II may not be strictly justified because the latter were calculated from the Curie law whereas the former were obtained from the Curie–Weiss law. In the former case θ, the Weiss constant, may be attributed reasonably to intermolecular interactions[1] but in the latter group of complexes the ground state is more complicated and the possibility of a slightly temperature dependent moment exists. This state of affairs does not make the evaluation of θ necessarily significant as a means of effecting a genuine comparison between the data of Parts I and II and those of Tables I and II. However, in the series prototype, CoA_2, evaluation of a Weiss constant

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(8) F. P. Dwyer and A. M. Sargeson, *J. Proc. Roy. Soc. N. S. Wales*, **90**, 29 (1956).

(9) C. J. Ballhausen and C. J. Jørgensen, *Acta Chem. Scand.*, **9**, 397 (1955).

(10) R. A. Holm and F. A. Cotton, to be published.

(11) (a) Spectral studies of a number of metal acetylacetonates of known structures lead to the conclusion that acetylacetonate oxygens provide a slightly stronger field than H_2O oxygens (Holm and Cotton, unpublished). (b) A tetrahedral $Co^{II}-O_4$ arrangement in 12-tungstocobaltate has been reported (L. C. W. Baker and V. E. Simmons, THIS JOURNAL, **81**, 4744 (1959)), but no magnetic data are as yet available.

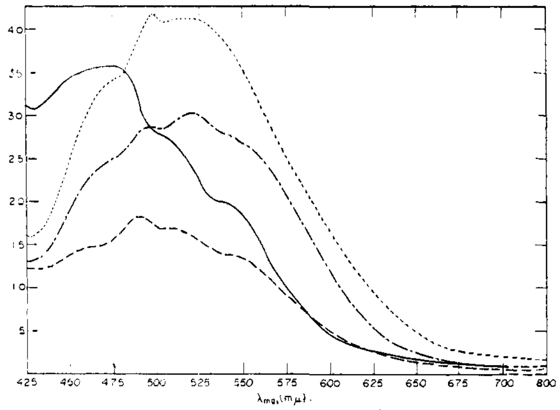

Fig. 1.—Solution spectra of Co(II) acetylacetonate in visible region: -------, benzene; ——, pyridine; — — — —, chloroform; ————, methanol.

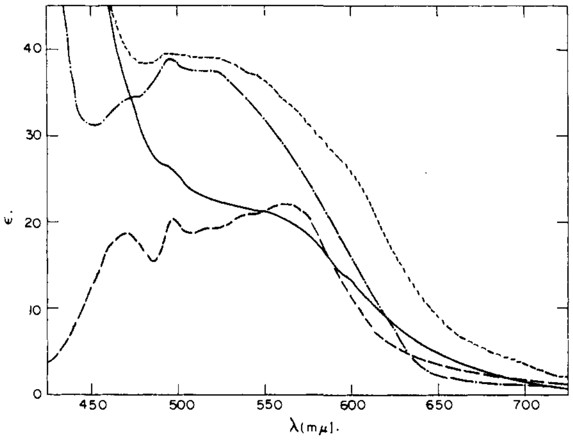

Fig. 2.—Spectra of some quadricoördinate spin-free Co(II) complexes: ——, bis-(benzoylacetonato)-Co(II) in benzene; ------, bis-(benzoylethylaceto)-Co(II) in benzene; —·—·, bis-(trifluoroacetylacetonato)-Co(II) in benzene; —————, bis-(S-ethylthioglycolato)-Co(II) in chloroform.

leads to an even higher moment thereby possibly accentuating the contrast. One interesting comparison that can be made in Tables I and II is the slight change in moment upon dehydration of a particular complex. $CoA_2 \cdot 2H_2O$ is known to have a tetragonal structure[12] with four equal bonds (2.05 Å.) to the chelate oxygens and two much longer bonds (2.23 Å.) to the water oxygens. It seems quite likely that the other hydrates with at least $2H_2O/Co$ are similarly constituted. It appears that the increase in the "tetragonality" of the ligand field on going from such dihydrates to the anhydrous compounds has an almost negligible effect upon the orbital contribution. This implies that the source of this orbital contribution is a ground state degeneracy which is a consequence of tetragonal symmetry irrespective of how marked the tetragonality may be.

A second line of evidence against a tetrahedral structure is the visible absorption spectra of CoA_2 in several solvents which are presented in Fig. 1. In Fig. 2 the spectra of several other members of the series are shown. The similarity of the spectra in benzene is clear and indicates that nearly the same ligand field strengths and symmetries exist in all compounds. The spectra which are shown in Figs. 1 and 2 are to be contrasted with the spectra of known tetrahedral complexes as given in Fig. 2 of Part I[1] and Fig. 5 of ref. 9. For more pertinent comparisons the spectra of two tetrahedral $Co-O_4$ complexes are given in Fig. 3. The spectrum of Co^{+2} in ZnO in which it occupies tetrahedral sites is presented in ref. 13. In no instance does the spectrum of any compound in Tables I and II possess any strong absorption bands in the 600–800 mμ region whereas all tetrahedral cobaltous complexes thus far examined[1,9,10,13] exhibit in this region a characteristic, intense, multicomponent band associated with the $^4A_2-^4T_1(P)$ transition in tetrahedral symmetry. Consequently, in view of the above, it is tempting to postulate a planar structure for the complexes of $Co-O_4$ series.

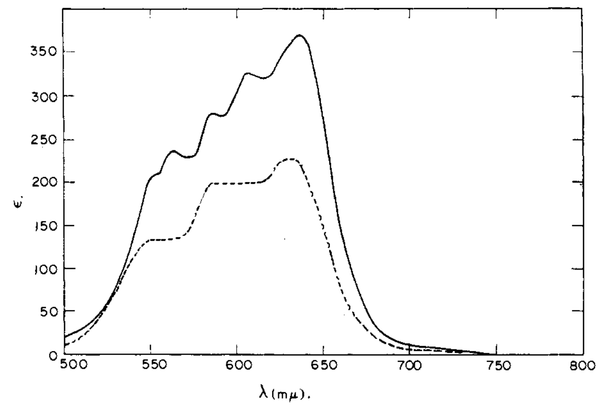

Fig. 3.—Spectra of two tetrahedral $Co-O_4$ complexes in nitromethane: ——, $Co(Ph_3PO)_4(ClO_4)_2$; ------, $Co(Me_3PO)_4(ClO_4)_2$.

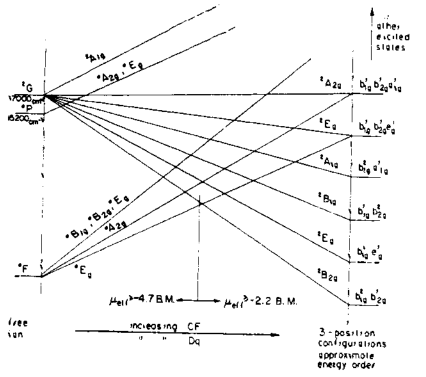

Fig. 4.—Simplified ligand field energy diagram for planar (D_{4h}) Co(II); configuration interaction is ignored; energy scales arbitrary; assumed energy $d_{z^2} < d_{xz}, d_{yz}$.

Up to this point the incompatibility of the magnetic and spectral data of these quadricoördinate complexes with the assumption of a tetrahedral configuration has been discussed but with little mention as to whether the data are compatible with a planar model. This point will now be pursued with the aid of simple ligand field theory. An energy level diagram for Co(II) in a ligand field of D_{4h} symmetry is shown in Fig. 4. This diagram was constructed by the use of the non-crossing rule and

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[12] G. J. Bullen, *Acta Cryst.*, **12**, 703 (1959).

[13] D. S. McClure, *Phys. and Chem. Solids*, **3**, 311 (1957).

standard group theoretical methods. The states in the limit of strong ligand field are derived by considering the d^7 configuration of Co(II) equivalent to a d^3 configuration with the energy order inverted. The order of several of the strong field levels is dependent on the assumption that in the limit of a very strong ligand field in which the tetragonal symmetry is very pronounced the energy of the d_{z^2} orbital is less than that of the degenerate pair d_{xz}, d_{yz}. It is to be emphasized that this diagram is not complete and illustrates the correlations with the limiting strong field states of some of the weak ligand field states arising from the ground state and first two excited states of the free ion. It is, however, only these states that are of primary chemical interest. Referring to Fig. 4, note that there is a discontinuity in the orbital symmetry and spin multiplicity of the ground state at some critical value of the ligand field strength. In the weaker field region the complexes are spin-free and in the stronger field region they are spin-paired. In the quadricoördinate spin-paired complexes mentioned at the outset, the donor atom sets of 4 N, 2 O and 2 N, 2 O and 2 S or 4 S evidently provide a ligand field strength exceeding that at the cross-over point and are undoubtedly planar. Certainly they are not tetrahedral because all tetrahedral cobaltous complexes must be spin-free (provided the energy levels are derived from $3d^7$ free ion configuration[1]). Judging from the position of oxygen-bearing ligands in the spectrochemical series, it is not surprising that a donor set of four oxygens could produce a ligand field of intensity insufficient to induce spin-pairing. The main conclusion to be drawn from Fig. 4 is that planar spin-free complexes are at least in principle possible if the four donor atoms provide a weak enough ligand field. This situation encountered here in the case of Co(II) is also present in Ni(II) where again in principle one can have a planar paramagnetic situation, although no such complex has been proven unambiguously to exist. Furthermore, all $Ni-O_4$ complexes are paramagnetic just as all $Co-O_4$ complexes are spin-free. For both metals the reduction in spin multiplicity and, presumably, the transition from planar spin-free to planar spin-paired complexes begins in the $M-O_2N_2$ and $M-O_2S_2$ series and almost always is complete in $M-N_4$, $M-N_2S_2$ and $M-S_4$ complexes.

In view of the non-conformity of the magnetic and spectral data of complexes of the $Co-O_4$ series to a tetrahedral configuration, it is strongly suggested that these complexes are planar. The large orbital contribution is not necessarily simply accounted for by a planar model, although if a ^4E state does lie lowest (Fig. 4) and is split only to an extent $\gtrsim kT$, one can predict qualitatively an orbital contribution but of uncertain magnitude. The objection might be raised that in the solid some or all of the anhydrous complexes are not truly quadricoördinate but that the metal is effectively six-coördinated to produce a z component to the tetragonal ligand field capable of effecting large orbital contributions such as we have found in the definitely tetragonal (*trans*) complexes $CoA_2 \cdot 2H_2O$,[12] $Co(OAc)_2 \cdot 4H_2O$[14] and $[Co(SC(NH_2)_2]_4Cl_2$[15] which have moments of 5.02, 5.16 and 4.90 B.M., respectively, at room temperature. However, CoA_2 is a monomer in dichloromethane and has the same absorption spectrum in this solvent as in the solid and in benzene where it possesses a moment of 4.81 B.M. No strong tetragonal field component can be present in benzene so that it is felt that the moment in this case at least is that attributable to a planar structure. Although the moment of CoA_2 in benzene is considerably less than that of the solid, it is still too large to be interpretable on a tetrahedral basis as is emphasized by the absorption spectrum of the complex in benzene. The same spectral and magnetic observations have been made for Co(II) trifluoroacetylacetonate in benzene. A number of spin-allowed transitions are seen to be possible from Fig. 4. The spectra of CoA_2 in chloroform and benzene (Fig. 1) and of other members of the series in benzene (Fig. 2) are not inconsistent with this possibility but do not necessarily support it. Further, it appears unlikely that CoA_2, in particular, is six-coördinated in chloroform and benzene because the spectra in pyridine and to a certain extent, in methanol, both coördinating solvents, are rather different from those in essentially non-coördinating solvents.

Measurements of the dipole moments of the bis-(trifluoroacetylacetonato) complexes of Be(II), Cu(II) and Co(II) also have been interpreted in favor of planar configurations for both of the latter, with about a 3:2 distribution in the *cis* and *trans* forms.[16]

Experimental

Magnetic Measurements.—The magnetic data on solids and solutions were obtained by the Gouy method as previously described.[1,2] For solution measurements the following gram susceptibilities were determined: Mallinckrodt reagent grade pyridine twice distilled from barium oxide, -0.619×10^{-6}; Baker reagent methanol once distilled from magnesium turnings, 0.670×10^{-6}; Fisher reagent chloroform, -0.496×10^{-6}; Fisher reagent benzene, -0.702×10^{-6}. The moments reported in Tables I and II are accurate to at least ± 0.05 B.M. The moments in solution refer to freshly prepared solutions. It was found that the moment of CoA_2 dissolved in non-outgassed solvents steadily decreased with time, the dependence of rate on solvent being $CHCl_3 > C_6H_5 > CH_3OH > py$; after two months the susceptibilities of 0.2–0.4 *M* solutions in benzene and chloroform had decreased below that for the spin-only value and the solutions gradually turned from violet to green. The pyridine solution did not undergo these changes and retained its moment of 4.82 B.M. after two months.

The rather sizable difference between the moment of solid CoA_2 calculated from the Weiss–Curie law and the moments in chloroform and benzene is outside the range of experimental error and cannot be accounted for unless initial oxidation in solution is quite rapid.

Spectral Measurements.—All spectra were recorded on freshly prepared solutions with a Cary recording spectrophotometer using matched quartz cells.

Molecular Weight.—The molecular weight of Co(II) acetylacetonate was determined isopiestically in dichloromethane. Calcd. for $Co(C_5H_7O_2)_2$: 245. Found: 260.

Preparation of Compounds. Bis-(acetylacetonato)-Co(II).—This compound was prepared according to the method of Charles and Pawlikowski[17] which yielded first the dihydrate.

Anal. Calcd. for $Co(C_5H_7O_2)_2 \cdot 2H_2O$: Co, 20.11; C, 40.98; H, 6.18. Found: Co, 19.9; C, 41.24; H, 6.39.

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[14] J. N. Van Niekirk and F. R. L. Schoening, *Acta Cryst.*, **6**, 609 (1953).

[15] L. Cavalca, M. Nardelli and A. Braibanti, *Gazz. chim. ital.*, **86**, 942 (1956).

[16] R. H. Holm and F. A. Cotton, *J. Inorg & Nuclear Chem.*, in press.

[17] R. G. Charles and M. A. Pawlikowski, *J. Phys. Chem.*, **62**, 440 (1958).

The dihydrate heated *in vacuo* for 6 hr. at 58° yielded the anhydrous compound, a purple crystalline material.

Anal. Calcd. for $Co(C_5H_7O_2)_2$: Co, 22.94; C, 46.71; H, 5.48. Found: Co, 22.8; C, 46.89; H, 5.56.

Bis-(salicylaldehyde)-Co(II).—The procedure of Tyson and Adams[18] led to an orange crystalline product, the dihydrate.

Anal. Calcd. for $Co(C_7H_5O_2)_2 \cdot 2H_2O$: Co, 17.48; C, 49.85; H, 4.18. Found: Co, 17.2; C, 49.97; H, 4.48.

By heating the dihydrate *in vacuo* for 12 hr. at 58°, the brown crystalline anhydrous compound was obtained.

Anal. Calcd. for $Co(C_7H_5O_2)_2$: Co, 19.57; C, 55.81; H, 3.35. Found: Co, 19.6; C, 55.71; H, 3.61.

Bis-(benzoylacetonato)-Co(II).—The compound was reported previously by Musante.[19] The orange-brown product was obtained by direct reaction of an aqueous solution of Co(II) acetate with an ethanolic solution of benzoylacetone; it was recrystallized twice from methanol–water to give yellowish crystals which readily lost water on standing. These crystals were completely dehydrated to the dark brown anhydrous compound by heating *in vacuo* at 80° for 24 hr.

Anal. Calcd. for $Co(C_{10}H_9O_2)_2$: Co, 15.46; C, 63.00; H, 4.76. Found: Co, 15.5; C, 62.95; H, 4.72.

Bis-(ethylbenzoylacetato)-Co(II).—Cobalt(II) acetate tetrahydrate (12.5 g.) was dissolved in 100 ml. of 50% ethanol to which was then added 19.1 g. of ethylbenzoylacetate. 3 *N* ammonia was added slowly until the solution was slightly basic. A yellowish product precipitated which was filtered off, washed well with water and ethanol and air-dried giving a light yellow powder.

Anal. Calcd. for $Co(C_{11}H_{11}O_3)_2 \cdot 2H_2O$: Co, 12.35; C, 55.35; H, 5.49. Found: Co, 12.3; C, 55.31; H, 5.58.

Heating *in vacuo* at 80° for 4 hr. produced the violet-brown anhydrous compound.

Anal. Calcd. for $Co(C_{11}H_{11}O_3)_2$: Co, 13.35; C, 59.87; H, 5.02. Found: Co, 13.1; C, 59.75; H, 4.93.

Bis-(guaiacolato)-Co(II).—The compound has been mentioned previously by Mellor and Craig.[20] 6.2 g. of cobaltous acetate tetrahydrate was dissolved in 100 ml. of 50% ethanol. To this solution was added 6.2 g. of guaiacol (*o*-methoxyphenol) in 100 ml. of ethanol and 6 *N* NH_3 was added slowly with stirring as a granular precipitate formed. The purple product was filtered off, washed well with water and ethanol and dried *in vacuo*.

Anal. Calcd. for $Co(C_7H_7O_2)_2$: Co, 19.31; C, 55.10; H, 4.62. Found: Co, 19.2; C, 54.96; H, 4.81.

Bis-(hexafluoroacetylacetonato)-Co(II) Hydrate.—The compound was obtained by direct reaction of an aqueous solution of cobaltous acetate with an ethanolic solution of hexafluoroacetylacetone. The orange crystalline product was twice recrystallized from ethanol–water.

Anal. Calcd. for $Co(C_5HF_6O_2)_2 \cdot 5/2H_2O$: Co, 11.36; C, 23.18; H, 1.36. Found: Co, 11.1; C, 23.10; H, 1.78.

The hydrate could not be dehydrated by heating *in vacuo* at 100° for 24 hr.

Bis-(trifluoroacetylacetonato)-Co(II).—The hydrate was obtained by a direct reaction similar to that used to prepare the hydrate of the hexafluoro compound.

Anal. Calcd. for $Co(C_5H_4F_3O_2)_2 \cdot 5/2\ H_2O$: Co, 14.37; C, 29.28; H, 3.19. Found: Co, 14.0; C, 29.48; H, 3.46.

The anhydrous compound was obtained from the hydrate as previously described.[16]

Bis-(tropolonato)-Co(II).—Tropolone was prepared according to the method of Doering and Knox.[21] The crude product was sublimed, m.p. 48–49°, lit. 49°; 1.06. g. of cobaltous acetate tetrahydrate was dissolved in 20 ml. of water and added slowly to a solution of 1.04 g. of tropolone in 30 ml. of 50% ethanol. A blood red precipitate formed which was filtered off, washed carefully with water, a small amount of 50% ethanol, ether and air-dried.

Anal. Found: C, 52.97; H, 3.69; corresponding closely to the monohydrate. Calcd. for $Co(C_7H_5O_2)_2 \cdot H_2O$: C, 52.68; H, 3.79.

This product was dried *in vacuo* at 58° for three days to give the deep red anhydrous compound.

Anal. Calcd. for $Co(C_7H_5O_2)_2$: C, 55.81; H, 3.25. Found: C, 55.77; H, 3.59.

Co(II) Kojate.—The compound was reported previously by Wiley, *et al.*[22]; 4.4 g. of cobaltous acetate tetrahydrate was dissolved in 25 ml. of water and to this solution was added 5 g. of sublimed kojic acid in 40 ml. of 50% ethanol. An orange precipitate slowly appeared. The solution was allowed to stand for 24 hr.; the orange product was filtered and washed thoroughly with water, ethanol and ether. A light orange powder resulted, insoluble in common noncoördinating solvents.

Anal. Found: C, 41.49; H, 3.29; Co, 16.5; agreeing best with $Co(C_6H_5O_4)_2 \cdot {}^1/_2H_2O$ for which, calcd.: C, 41.16; H, 3.17; Co, 16.76.

The water could not be removed by heating *in vacuo* at 100° for 24 hr.

Acknowledgments.—We are grateful to the National Science Foundation and the U. S. Atomic Energy Commission (Contract AT(30-1)-1956) for financial support and to the General Electric Company for a Charles Coffin Fellowship to R. H. H.

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Magnetic Evidence Indicative of Structures and Structural Changes in Complexes of Cobalt(II)

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It is observed that the literature now contains data and generalizations relating to the magnetic properties of a number of basic kinds of cobaltous complexes. It is shown that in this context magnetic data reported for bis-(*p*-toluidine)-cobalt(II) thiocyanate as a solid and in several solvents and for several isonitrile complexes of Co(II) can be used to infer certain features of stereochemistry and changes in stereochemistry of these substances.

Recent studies in this Laboratory have established that the magnetic behavior of tetrahedral cobaltous complexes is in good accord with the general pattern to be expected from ligand field theory and, furthermore, semi-quantitative correlations have been established between magnetic moments of such complexes and the positions of the ligands in the spectrochemical series.[1,2] It has

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