TABLE IV

EFFECT OF VARYING F

Complex	F	q	Δ, cm.$^{-1}$
$[Cr(NH_3)_6]^{3+}$	1.82	0.506	20,550
	2.00	0.449	24,050
	2.10	0.417	27,400
	2.20	0.388	29,460
	2.30	0.360	31,490
$[Co(NH_3)_6]^{3+}$	1.82	0.486	14,520
	2.00	0.442	16,920
	2.10	0.417	18,200
	2.20	0.393	19,530
	2.30	0.371	20,740
$[Co(NH_3)_6]^{2+}$	1.82	0.366	9,720
	2.00	0.320	11,060
	2.10	0.297	11,840
	2.20	0.275	12,640
$[Ni(NH_3)_6]^{2+}$	1.82	0.257	8,580
	2.00	0.211	9,750
	2.10	0.187	10,400
	2.20	0.163	11,090

using the ammonia IP, both for the reasons outlined above from a conceptual standpoint and because it appears that a smaller variation of F will be necessary to achieve correct results for all complexes.

Finally, we turn to the effect of varying F. In these calculations, all factors except F have been held constant. The ammonia diagonal element was taken to be the ionization potential of the ammonia molecule, with the charge dependence of $-84{,}000$ cm.$^{-1}$ decided on above. The results are presented in Table IV.

One conclusion is immediately obvious, indeed it was obvious in some of the calculations of Tables II and III. The implicit assumption that a single F will suffice for all calculations, even for a single type of overlap, is simply not true. To obtain correct, or even approximately correct, results it has been necessary to go from $F = 1.82$ for the $[Cr(NH_3)_6]^{3+}$ to $F = 2.30$ for $[Co(NH_3)_6]^{3+}$, and the latter value is still somewhat small. It is apparently not even possible to use a single F to obtain correct results for one metal, as $F = 2.00$ gives the best agreement with experiment for the cobalt(II) complex, whereas $F = 2.30$ or a slightly larger value is necessary to give approximate agreement for the cobalt(III) complex. For the nickel complex, either $F = 2.10$ or $F = 2.20$ gives agreement to within 300 cm.$^{-1}$ with the experimental value.

A trend is obvious in these results. The F necessary to achieve correct results increases as one passes through the first transition series. This trend is just the opposite of that found for the overlap integrals involving the 3d orbitals and suggests that in fact the magnitude of the off-diagonal elements may remain fairly constant across the series. It is interesting that this effect is precisely that found to be so very useful in the simple Hückel MO treatments of π-electron systems in conjugated organic molecules.

A comparison of the results for the cobalt(II) and cobalt(III) systems is of interest in still another connection. For a given F, the MWH method does predict a considerably smaller Δ for the cobalt(II) complex than for the cobalt(III) complex, in agreement with the observed fact that trivalent Δ are always considerably larger than divalent Δ. On the other hand, the magnitude of the difference is too small, Δ for the divalent complex being about two-thirds that for the trivalent compound, whereas it is observed to be approximately one-half. Thus, although the qualitative prediction is correct, the quantitative result leaves something to be desired. This can, of course, be overcome by the use of different values of F, as shown.

CONTRIBUTION FROM THE DEPARTMENTS OF CHEMISTRY, GEORGIA INSTITUTE OF TECHNOLOGY,
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Cyclohexylaminebis(pentane-2,4-diono)cobalt(II): Existence of Monomer and Dimer

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Methods of preparing the 1:1 adduct of bis(pentane-2,4-diono)cobalt(II) and cyclohexylamine are reported. Molecular weight data indicate the presence of a dimer in carbon tetrachloride and a monomer in chloroform; molecular weight and spectral data for benzene solutions of the compound are shown to be consistent with a monomer–dimer equilibrium.

Introduction

Various complexes of bis(pentane-2,4-diono)metal(II) compounds (hereafter abbreviated MA_2) with amines have been reported in the literature. Many diamine complexes have been isolated as solids and are analogous to the common diaquo complexes. Recently, Fackler obtained evidence for pyridine (abbreviated py in formulas) complexes of the formula $(MA_2)_2$py from spectrophotometric studies on solutions, using either cobalt(II)[2] or nickel(II)[3] as metal ion. He was also able to isolate the solid compounds, but did not report any data other than analyses for the solids. In addition, Fackler found evidence for a

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[1] N.S.F. Faculty Research Participant, Georgia Institute of Technology, 1963.

[2] J. P. Fackler, Jr., *Inorg. Chem.*, **2**, 266 (1963).

[3] J. P. Fackler, Jr., *J. Am. Chem. Soc.*, **84**, 24 (1962).

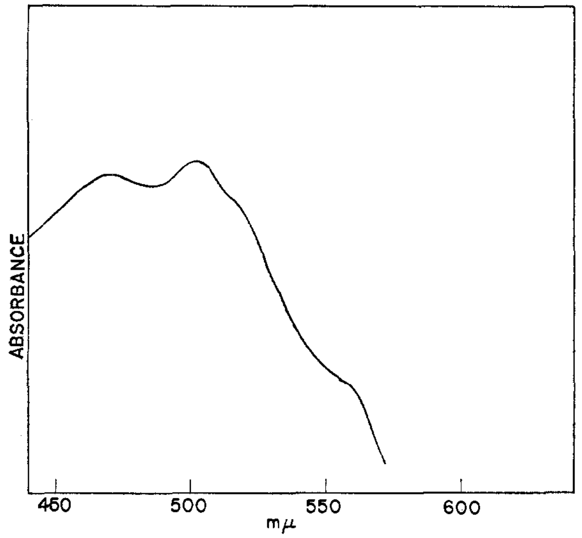

Fig. 1.—Spectrum of solid $CoA_2(Cha)$, as mull in Nujol. The absorbance scale is arbitrary.

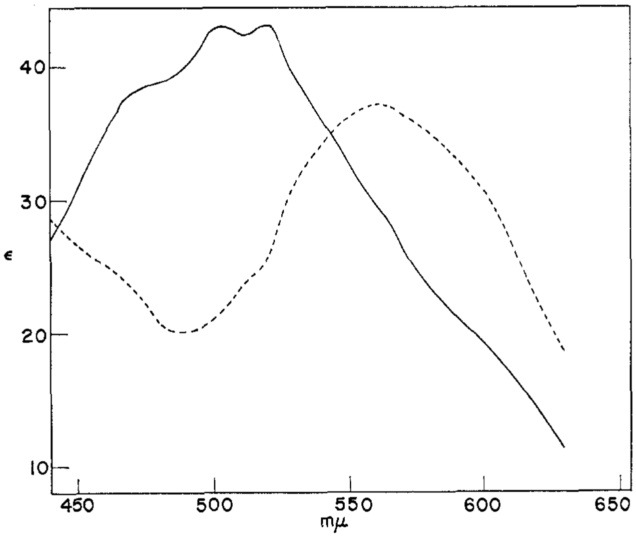

Fig. 2.—Spectra obtained for solutions of $CoA_2(Cha)$: ———, carbon tetrachloride as solvent; --------, chloroform as solvent.

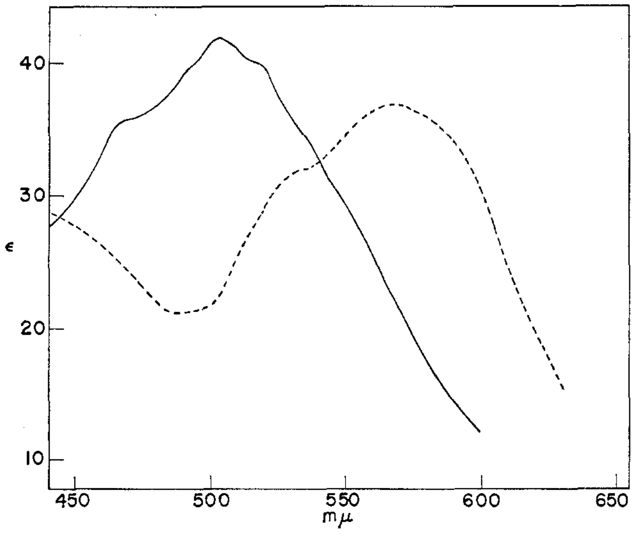

Fig. 3.—Spectrum of monomer and dimer as calculated from the equilibrium in benzene: ———, dimer; ---------, monomer.

species, CoA_2py, in solution, but did not isolate the complex.[3] Complexes of the same stoichiometry had previously been reported by Graddon on the basis of spectrophotometric studies on the systems NiA_2 with 4-methylpyridine[4] and CuA_2 with pyridine[5]; solids were not isolated.

We have obtained the complex $CoA_2(Cha)$ (in formulas, Cha represents cyclohexylamine) by thermal decomposition of the diamine complex, $CoA_2(Cha)_2$, and by crystallization from a concentrated benzene solution containing CoA_2 and cyclohexylamine in a 1:1 ratio.

Experimental

Bis(pentane-2,4-diono)cobalt(II).—This compound was prepared according to literature methods[6] and recrystallized from methanol.

Bis(cyclohexylamine)bis(pentane-2,4-diono)cobalt(II).—CoA_2 was dissolved in methanol and treated with a solution of cyclohexylamine in methanol to give an amine to cobalt ratio of 2:1. A pale, orange-pink solid rapidly separated and was filtered and dried under vacuum over sulfuric acid. Recrystallization from methanol yielded fine, needle crystals.

Anal. Calcd. for $CoC_{22}H_{40}O_4N_2$: C, 58.02; H, 8.80. Found: C, 58.5; H, 8.7.

Cyclohexylaminebis(pentane-2,4-diono)cobalt(II).—This compound has been prepared by two different methods.

Method 1.—$CoA_2(Cha)_2$ was placed in a drying pistol, heated to 100°, and maintained at oil pump pressure (~0.01 mm.). The orange-pink needles slowly became deep red. After 24 hr., conversion appeared complete; a sample was taken for analysis and the remainder was heated at 100° under vacuum for an additional 24 hr., and a second sample was then taken for analysis. The two samples gave identical analyses.

Anal. Calcd. for $CoC_{16}H_{27}O_4N$: C, 53.93; H, 7.58; N, 3.63. Found: C, 54.0, 53.9; H, 7.7, 7.7; N, 3.9, 3.6.

Method 2.—CoA_2 was dissolved in a minimum amount of hot benzene, and an equimolar amount of cyclohexylamine was slowly added. A small amount of orange-pink crystals formed on mixing, but on standing for several hours, deep red crystals began to separate. The solid was separated by filtration, washed several times with benzene to remove small amounts of the orange-pink solid, and then dried over sulfuric acid.

Anal. Found: C, 54.1; H, 7.4.

Molecular Weight Measurements.—The molecular weight of $CoA_2(Cha)$ was determined in dichloromethane by the isopiestic method. For the same compound, the molecular weight was determined in chloroform, carbon tetrachloride, and benzene with a Mechrolab, Inc., vapor pressure osmometer, calibrated with biphenyl. The results are summarized in Table I.

Table I

Molecular Weight Data for $CoA_2(Cha)$

Solvent	Apparent mol. wt.
Chloroform	370
Carbon tetrachloride	640
Benzene	520[a]
Dichloromethane	450[b]

[a] 0.012 *M* solution. [b] Isopiestic method.

Spectral Studies.—Visible spectra were measured using a Bausch and Lomb Spectronic 505 spectrophotometer. The spectrum of solid $CoA_2(Cha)$ was obtained using a mull in Nujol.

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(4) D. P. Graddon and E. C. Walton, *Nature*, **190**, 906 (1961).

(5) D. P. Graddon, *ibid.*, **183**, 1610 (1959).

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

Magnetic Measurements.—The magnetic susceptibility (10,213 × 10^{-6} c.g.s. unit) of $CoA_2(Cha)$ was determined by the Gouy method at 25°, using $HgCo(CNS)_4$ as a calibrant. A correction for diamagnetism (187 × 10^{-6} c.g.s. unit) was made using Pascal's constants. The value of μ_{eff} was found to be 5.0 B.M.

Results and Discussion

The molecular weight measurements, Table I, indicate that $CoA_2(Cha)$ exists primarily as a dimer in carbon tetrachloride and as a monomer in chloroform. Comparison of the spectra of the solid, Fig. 1, and of solutions, Fig. 2, then indicates that the dimer is present in the solid.

The molecular weight measurements in benzene solution indicate an equilibrium between the monomer and dimer with an equilibrium constant for the reaction

$$[CoA_2(Cha)]_2 \rightleftharpoons 2CoA_2(Cha)$$

of approximately 4 × 10^{-3} at 37°. Using this value, the fractions of monomer and dimer were found for several solutions of different concentrations. By a method of least-squares fitting, the extinction coefficient of each species was computed at 10 mμ intervals to obtain the spectra shown in Fig. 3. Comparison with Fig. 2 shows good agreement and indicates that these are probably the only important species present.

Since Fackler had found evidence for a 1:1 complex in his studies but had not isolated such a complex, we attempted to prepare CoA_2py by the methods used for $CoA_2(Cha)$ to see if similar spectral results could be obtained for the pyridine system. Method 1 gave only CoA_2, both pyridine molecules being removed even at temperatures lower than 100°; method 2 gave only $(CoA_2)_2py$ as reported by Fackler.[2] The spectrum of a Nujol mull of this compound was the same as reported by Fackler for the solution and very similar to the dimer spectrum of $[CoA_2(Cha)]_2$.

These results indicate that the nature of the amine has a large effect on the equilibria involved in an amine–MA_2 system. The same dependence on the nature of the amine probably accounts for the seeming discrepancy in the results of Fackler,[3] who reported $(NiA_2)_2$(amine), using pyridine as amine, and Graddon,[4] who reported NiA_2(amine), using methylpyridines.

Comparison of the spectra of CoA_2 (at higher concentrations), $[CoA_2(Cha)]_2$, and $CoA_2(Cha)_2$ shows a slight shift to higher energy with the addition of amine; the spectra are similar, although the diamine has lower extinction coefficients. The spectra are indicative of "octahedral" coordination with the remaining positions of CoA_2 and $[CoA_2(Cha)]_2$ being filled through molecular association as discussed recently[7] for $(CoA_2)_x$. A possible structure for the dimer, $[CoA_2(Cha)]_2$, is shown in Fig. 4.

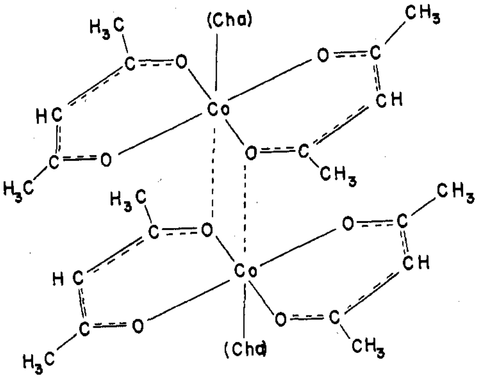

Fig. 4.—A possible structure for the dimer, $[CoA_2(Cha)]_2$.

The spectrum of the monomer, $CoA_2(Cha)$, is also similar, but shifted to much lower energy. This may indicate that the symmetry is essentially the same for the cobalt ion in the monomer and dimer, with the ligand field of the monomer being reduced due to the lower coordination number. The monomer may have a five-coordinate square-pyramidal structure, but the possibility of a trigonal bipyramidal structure, or one intermediate between these, such as that found[8] for $ZnA_2 \cdot H_2O$, is not excluded by any available data.

In view of the existing uncertainty about the structures of $[CoA_2(Cha)]_2$ and $CoA_2(Cha)$, detailed discussion of the spectra would be premature. It may be said, however, that the spectrum of the dimer can be reasonably assigned as a "$4T_1(F) \rightarrow 4T_1(P)$" transition of an "octahedrally" coordinated cobalt(II) ion, broadened and split by deviations from O_h symmetry. The band lies at a somewhat higher energy than those[7] for $(CoA_2)_x$ or $CoA_2(H_2O)_2$ because one of the six ligand atoms is nitrogen instead of oxygen. It has been observed that the red crystals of $[CoA_2(Cha)]_2$ are markedly dichroic; upon completion of a crystal structure determination now in progress, this and other features of the spectrum will be more thoroughly investigated.

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[7] F. A. Cotton and R. H. Soderberg, *Inorg. Chem.*, **3**, 1 (1964).

[8] H. Montgomery and E. C. Lingafelter, *Acta Cryst.*, **16**, 748 (1963).