phinate anion whose metal derivative was the only species isolated.

Acknowledgment.—We wish to thank Professor Richard C. Lord, Massachusetts Institute of Technology, for making his PE 521 available to us and to Professor Samuel O. Grim, University of Maryland, for running the ^{31}P nmr spectra.

Five-Coordinate, Square-Pyramidal Chelate Complexes of a Novel Tetradentate Amino Acid Like Ligand

BY DONALD F. AVERILL, J. IVAN LEGG,* AND DAVID L. SMITH[1]

The chemistry of a novel tetradentate aminecarboxylic acid ligand, 1,5-diazacyclooctane-N,N'-diacetate (dacoda), is reported. Due to the steric makeup of its chelates, an alkyl proton effectively blocks a coordination site on the metal ion which allows the coordination of only one additional ligand. Consequently a five-coordinate, square-pyramidal complex results. The complexes [M(dacoda)(H$_2$O)] (M^{2+} = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}) were prepared, and their spectroscopic and magnetic properties were compared with those of the octahedral, diaquo complexes of ethylenediamine-N,N'-diacetate (EDDA), a ligand of comparable crystal field strength. The five-coordinate nature of [M(dacoda)(H$_2$O)] (M^{2+} = Co^{2+}, Ni^{2+}) both in the solid state and in aqueous solution was established by comparison of X-ray powder patterns and solid and solution spectra. The Zn^{2+} complex is isomorphous. The crystal structure of the Ni(II) complex has been determined in this laboratory. The Co(II)–dacoda complex is stable to oxidation under conditions normally employed to obtain facile oxidation of amino acid–cobalt(II) complexes.

Introduction

A useful classification of five-coordinate complexes is in terms of the ligand field strength of the ligands involved.[2] With one exception[3] these complexes are unstable in strong polar solvents and as a consequence many of them have to be prepared under anhydrous conditions.

We have synthesized a tetradentate amino acid like ligand, 1,5-diazacyclooctane-N,N'-diacetate (dacoda), which forms five-coordinate, square-pyramidal complexes in aqueous solution and the solid state.[4] This geometry has been established for the Ni(II) complex by an X-ray crystal structure determination.[5] The design of dacoda, Figure 1, was predicated on the stereochemical nature of chelates formed with the parent amine 1,5-diazacyclooctane (daco).[6] The key to the design of ligands which would lead to five-coordinate, square-pyramidal complexes was to take advantage of the unique mode of coordination of daco. When daco is coordinated, a proton on the 3 carbon (or 7 carbon) is forced over the metal ion in order to avoid steric crowding with a proton on the 7 carbon (or 3 carbon), Figure 1. This blocks this position to further coordination. The two six-membered chelate rings of the bicyclic ring system define a chair and boat conformation. Musker and Hussain took advantage of this predicted behavior to prepare square-planar M(daco)$_2^{2+}$ complexes where a proton from each daco blocks an apical position on the octahedron.

By alkylating one or both of the ring nitrogens of daco with a group containing a coordinating ligand, a complex with only one daco unit is anticipated since only one ligand is expected to coordinate. Thus only one position is blocked and a five-coordinate complex is expected to form. Furthermore, the N-R substituents must coordinate in the plane of the nitrogens, and consequently the complexes will be square pyramidal.

We have synthesized a series of N-substituted ligands of daco and its closely related homolog 1,4-diazacycloheptane (dach, homopiperazine) most of which are expected to form five-coordinate complexes. The ligands are relatively simple, lacking bulky, dangling groups such as phenyl or ethyl and uncomplicated by the presence of π-acceptor ligating atoms. Hydrolysis under neutral or near-neutral conditions is not anticipated, and thus the geometry should be maintained under aqueous conditions. Our interest in these ligands is related to both the unique stereochemistry involved and the expected behavior of certain of these complexes as models for metalloproteases. This report is concerned with the Co(II), Ni(II), Cu(II), and Zn(II) complexes of 1,5-diazacyclooctane-N,N'-diacetate, dacoda. The properties of these complexes were compared with the complexes of ethylenediamine-N,N'-diacetate (EDDA), a ligand of similar crystal field strength which was expected to lead to the formation of normal six-coordinate complexes.

Experimental Section

Preparation of Ligands.—Ethylenediamine-N,N'-diacetic acid (H$_2$EDDA) was obtained from K & K Laboratories and was used as received. A previously reported procedure[7] was used to prepare 1,5-diazacyclooctane (daco) and the product was purified as the dihydrobromide salt.[8]

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(1) National Science Foundation Undergraduate Research Participant.
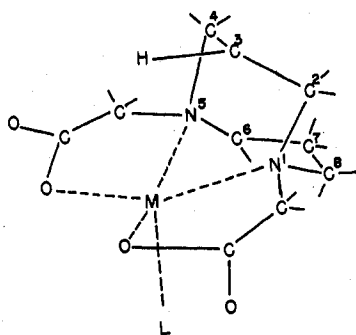
(2) L. Sacconi, *J. Chem. Soc. A*, 248 (1970).

(3) M. Ciampolini and P. Paoletti, *Inorg. Chem.*, **6**, 1261 (1967), and references therein.

(4) For a preliminary report see J. I. Legg, D. O. Nielson, D. L. Smith, and M. L. Larson, *J. Amer. Chem. Soc.*, **90**, 5030 (1968).

(5) D. O. Nielson, M. L. Larson, R. D. Willett, and J. I. Legg, *ibid.*, **93**, 5079 (1971).

(6) W. K. Musker and M. S. Hussain, *Inorg. Chem.*, **5**, 1416 (1966).

(7) E. L. Buhle, A. M. Moore, and F. G. Wiseloge, *J. Amer. Chem. Soc.*, **65**, 29 (1943).

(8) J. H. Billman and L. C. Dorman, *J. Org. Chem.*, **27**, 2419 (1962).

Figure 1.—The stereochemistry of M(dacoda)(L).

Barium 1,5-diazacyclooctane-N,N'-diacetate was prepared using a method previously reported for the alkylation of amines.[9] However, occasionally contamination of the product with $BaCO_3$ was encountered. It is suggested, then, that the synthesis be carried out in the absence of air. *Anal.* Calcd for [$BaC_{10}H_{16}N_2O_4$]·$2H_2O$: C, 29.89; H, 5.02; N, 6.98. Found: C, 29.84; H, 4.72; N, 7.14.

Preparation of Complexes of 1,5-Diazacyclooctane-N,N'-diacetate (dacoda).—The preparation of [Co(dacoda)H_2O]·$2H_2O$ is described below. The preparation of the corresponding Ni(II) and Cu(II) complexes was the same except that 0.655 g of $NiSO_4$·$6H_2O$ and 0.621 g of $CuSO_4$·$5H_2O$ were used for the respective syntheses.

To a stirred slurry of 1.00 g (0.00250 mol) of Ba(dacoda)·$2H_2O$ in 20 ml of water at 50° was added dropwise a solution of 0.715 g (0.00250 mol) of $CoSO_4$·$7H_2O$ in 15 ml of water. After cooling, the $BaSO_4$ was removed. Evaporation to dryness under vacuum produced a crop of violet crystals. The crystals were broken up in 50% ethanol–water, filtered, and washed with 95% ethanol. The air-dried yield was 0.65 g, 77%. The product was further dried over $CaSO_4$. The analyses for this complex and the other complexes prepared are given in Table I. The yields were about 70%.

TABLE I
ANALYTICAL DATA

Complex	Color	% calcd C	H	N	% found C	H	N
Hydrated dacoda Complexes							
$C_{10}H_{22}N_2O_7Co$	Violet	35.21	6.51	8.21	35.33	6.35	8.09
$C_{10}H_{22}N_2O_7Ni$	Blue-green	35.23	6.51	8.21	35.36	6.34	7.87
$C_{10}H_{22}N_2O_7Cu$	Dark blue	34.74	6.42	8.10	34.92	6.01	7.91
Anhydrous Ni(dacoda)							
$C_{10}H_{16}N_2O_4Ni$	Yellow-orange	41.85	5.61	9.77	41.72	5.46	9.87
EDDA Complexes							
$C_6H_{16}N_2O_7Co$	Pink	25.10	5.62	9.76	25.58	5.87	9.61
$C_6H_{14}N_2O_6Ni$	Light blue	26.80	5.25	10.42	26.72	5.15	10.61
$C_6H_{16}N_2O_7Cu$	Dark blue	24.70	5.53	9.60	24.81	5.81	9.75

From the green [Ni(dacoda)(H_2O)]·$2H_2O$ the orange, square-planar complex could be prepared by heating the green crystals *in vacuo* at 150° for 8 hr. This complex could also be prepared by breaking up and stirring the green complex in absolute ethanol.

Preparation of Complexes of Ethylenediamine-N,N'-diacetate (EDDA). (a) **Ethylenediamine-N,N'-diacetato(diaquo)cobalt(II) Hydrate.**—The reaction was carried out in a three-necked flask using deaerated water. The flask was flushed with nitrogen throughout the reaction. During the filtrations nitrogen was drawn through the filter through a sealed connection. These measures did not completely prevent contact with the air but were sufficient to prevent oxidation of the

(9) F. L. Garvan in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor, Ed., Academic Press, New York, N. Y., 1964, p 285; J. I. Legg and D. W. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).

cobalt(II) complex as evidenced by darkening of the product when these precautions were not taken. To a stirred slurry of 1.31 g of $CoCO_3$ (0.0100 mol) in 30 ml of water was added 1.76 g of H_2EDDA. The reaction was heated (60°) until evolution of CO_2 was complete (10 min), and the mixture was filtered rapidly through a medium-fritted disk. The solution was placed in a vacuum desiccator which was evacuated until a large crop of pink crystals formed. The product was filtered and washed with two 5-ml portions of ice-cold water, alcohol, and acetone. After drying in the filter with nitrogen the yield of [Co(EDDA)(H_2O)$_2$]·H_2O was 0.8 g, 30%. The dried product appeared to be stable in air.

(b) **Preparation of Ethylenediamine-N,N'-diacetato(diaquo)nickel(II).**—To a slurry of 1.76 g (0.0100 mol) of H_2EDDA in 40 ml of water on a steam bath were added 2.62 g (0.0110 mol) of $NiCl_2$·$6H_2O$ and 0.8 g (0.2 mol) of NaOH with stirring. The solution was evaporated to about 10 ml on a steam bath, cooled, and filtered. The crude product was washed with ethanol to give 1.30 g. This was dissolved in a minimum amount of water (20 ml) at 70°. After cooling, filtering, and washing as before, 1 g of light blue crystals was obtained. The air-dried yield was 37%.

(c) **Preparation of Ethylenediamine-N,N'-diacetato(diaquo)copper(II) Hydrate.**—To a slurry of 1.21 g (0.00250 mol) of $CuCO_3$·$Cu(OH)_2$ in 25 ml of water on a steam bath was added 1.76 g (0.0100 mol) of H_2EDDA. The mixture was heated (until the evolution of CO_2 ceased), filtered, and evaporated to about 5 ml. The viscous mixture was filtered, and the deep blue precipitate was washed with ethanol and air-dried; yield 0.50 g (31%).

Physical Measurements.—The solution ((0.5–1) × 10^{-3} M for the dacoda complexes and 4 × 10^{-2} M for the EDDA complexes) absorption spectra were obtained with a Cary Model 14 spectrophotometer. The spectrum of orange Ni(dacoda) was obtained in nitromethane. Solid-state transmittance spectra were obtained either by mounting single crystals over a small aperature on a metal disk or by mulling the sample in hexachlorobutadiene or Nujol and "painting" filter paper which was held by clamped wooden plates cut to fit the sample holder. The results obtained by either method were essentially the same. The spectrum of Zn(dacoda)(H_2O) which is transparent in the near-uv and visible spectrum was used to estimate the scattering background in the spectra of the Ni(II) and Co(II) analogs. Powder patterns were obtained using Cu Kα radiation. Infrared spectra in the solid state were recorded on a Perkin-Elmer 700 infrared spectrophotometer using KBr disks or Nujol mulls. Aqueous solution spectra were obtained in D_2O. Temperature-dependent (77–298°K) magnetic susceptibilities were obtained by the Faraday method using a Cahn RG automatic electrobalance and a Varian V-4005 4-in. electromagnet. The cryostat unit employed was designed by University Research Glassware. Analyses were performed by Galbraith Laboratories, Inc., and by Alfred Bernhardt Mikroanalytisches Laboratorium.

Results and Discussion

The Nickel(II) Complexes.—The use of EDDA afforded a standard by which deviations form an octahedral arrangement of ligands could be monitored. Al-

TABLE II
ELECTRONIC ABSORPTION SPECTRA AND ASSIGNMENTS FOR THE
NICKEL(II) AND COBALT(II) COMPLEXES

Ni(EDDA)(H_2O)$_2$ ν, kK	Calcd ν, kK[a]	Assignment, O_h	Ni(dacoda)(H_2O) ν, kK	Assignment, C_{4v}[c]
9.90 (12.6[b])		$^3A_{2g} \rightarrow {}^3T_{2g}$	12.3 (21.4)	$^3B_1 \rightarrow {}^3A_2$
13.2 (1.9)		$\rightarrow {}^1E_g$	13.1 (25.3)	$\rightarrow {}^3B_2$
16.4 (4.2)	16.2	$\rightarrow {}^3T_{1g}(F)$	15.8 (28.0)	$\rightarrow {}^3E(F)$
27.2 (7.2)	27.4	$\rightarrow {}^3T_{1g}(P)$	26.4 (86.5)	$\rightarrow {}^3E(P)$

Co(EDDA)(H_2O)$_2$ ν, kK	Assignment, O_h	Co(dacoda)(H_2O) ν, kK
8.95 (6.0)	$^4T_{1g} \rightarrow {}^4T_{2g}$	8.05 (7.0)
19.9 (11.7)	$\rightarrow {}^4T_{1g}(P)$	18.2 (32.0)
		22.0 (22.5)

[a] See Text. [b] Molar absorptivity, ϵ, M^{-1} cm^{-1}. [c] These are tentative assignments at best since the energy-level diagram for d^8 in C_{4v} is complex, and the energies of the states are sensitive to relative changes in the in-plane and axial fields. See ref 14.
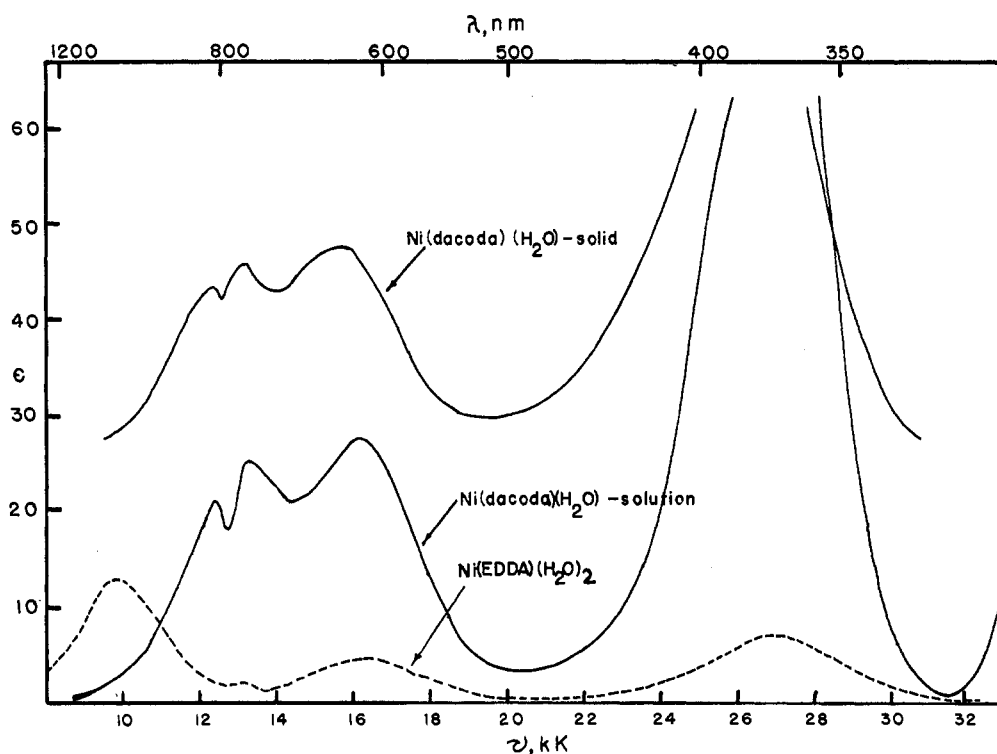
Figure 2.—The electronic absorption spectra of the nickel(II) complexes. Relative absorbance is shown for the solid-state spectrum.

though EDDA has two secondary amines whereas dacoda has two tertiary amines, both incorporate two glycinate units into an alkyl backbone and are consequently expected to be close in the spectrochemical series. The electronic absorption spectrum of Ni-(EDDA)(H$_2$O)$_2$ is recorded in Figure 2. The spectrochemical behavior of nickel complexes often reflects the average coordination geometry. That such is the case for Ni(EDDA)(H$_2$O)$_2$ (probably *cis*-diaquo) is demonstrated by the calculation of the energies of the $^3A_{2g} \rightarrow$ $^3T_{1g}$(F) and $^3A_{2g} \rightarrow$ $^3T_{1g}$(P) transitions from the $^3A_{2g} \rightarrow$ $^3T_{2g}$ transition which has an energy of $10Dq$.[10] The close agreement (within 2%) between the observed and calculated values, Table II, gives strong support for the expected octahedral geometry of Ni(EDDA)-(H$_2$O)$_2$. The band assignments are summarized in Table II. The effective magnetic moment, 3.21 BM, is within the range expected for octahedral Ni(II) complexes.[11]

The dacoda–Ni(II) complex gives rise to a greenish blue solution in water similar in appearance to that found for the EDDA complex, but the electronic absorption spectra of the two complexes, Figure 2, differ markedly. The significantly greater molar absorptivity of the dacoda complex suggests a much lower symmetry. [Ni(dacoda)(H$_2$O)]·2H$_2$O has been shown to be square pyramidal in the solid state.[5] The direct correlation between the solid and solution spectra, Figure 2, establishes a square-pyramidal, five-coordinate geometry for this complex in water. Furthermore, H$_2$^{17}O broad-line nmr studies strongly support the presence of only one exchangeable water, and pH titrations give no indication of uncoordinated carboxylates above pH 4.[12]

The asymmetric carbonyl stretching modes of ligand carboxylates have been used to determine the environment of this functional group.[13] In general the following have been found: protonated carboxylate, >1700 cm^{-1}; coordinated carboxylate, 1650–1600 cm^{-1} (in a few cases lower); ionic carboxylate, <1600 cm^{-1}. Infrared spectra were obtained both in the solid state and in D$_2$O (to eliminate interference from OH) and are summarized in Table III. These data support fully

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TABLE III
ASYMMETRIC CARBONYL STRETCHING MODES (CM^{-1})
FOR dacoda AND ITS COMPLEXES

	Solid	Soln (D$_2$O)
[Ni(dacoda)(H$_2$O)]·2H$_2$O	1620	1600
[Co(dacoda)(H$_2$O)]·2H$_2$O	1620	1600
[Cu(dacoda)(H$_2$O)]·2H$_2$O	1630	1610
[Zn(dacoda)(H$_2$O)]·2H$_2$O	1590	1600
Ba(dacoda)·2H$_2$O	1570	1440

</div>

coordinated carboxylates in both states for the Ni(II) complex.

Ciampolini has calculated in some detail the behavior of the d^8 electronic states in C_{4v} symmetry (square-pyramidal field) as the various geometric parameters are varied.[14] He found that the energy of the states is very sensitive to variation of the metal ion position with respect to the plane and to variation of axial ligand field. The holohedrized symmetry[15] of Ni(dacoda)H$_2$O is C_{4v}. The tentative assignment of the transitions on the basis of this symmetry using Ciampolini's calculated energy-level diagrams as a guide are given in Table II.

The gram magnetic susceptibilities of [Ni(dacoda)-

(10) W. C. E. Higginson, S. C. Nyburgh, and J. S. Wood, *Inorg. Chem.*, **3**, 463 (1964).

(11) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 37 (1964).

(12) J. S. Frye and J. P. Hunt, unpublished results.

(13) R. E. Sievers and J. C. Bailar, Jr., *Inorg. Chem.*, **1**, 174 (1962), and references therein.

(14) M. Ciampolini, *ibid.*, **5**, 35 (1966).

(15) C. E. Schäffer and C. K. Jørgensen, *Kgl. Dan. Vidensk. Selsk., Mat.-Fys. Medd.*, **29** (14) (1955); *Chem. Abstr.*, **49**, 10725c (1955).

TABLE IV
MAGNETIC DATA FOR dacoda COMPLEXES

Complex	$10^6\chi_g(20°) \pm \sigma$, emu/g	N^a	C, emu deg/g	Θ, °C	μ_{eff}, BM 77°K	μ_{eff}, BM 293°K
Co(dacoda)·3H$_2$O	28.46 ± 0.32	10	3.23	−24	4.60	4.81
Ni(dacoda)·3H$_2$O	13.09 ± 0.07	10	1.44	−14	3.12	3.30
Cu(dacoda)·3H$_2$O	3.94 ± 0.05	10	0.47	−13	1.83	1.90
Ni(en)$_3$S$_2$O$_3$^{b} (std)	11.07 ± 0.13	10				

^{a} Number of measurements of χ_g. ^{b} The literature value for this compound is $\chi_g(20°) = 11.30 \times 10^{-6}$ emu/g ± 1%: N. F. Curtis, *J. Chem. Soc.*, 3147 (1968).
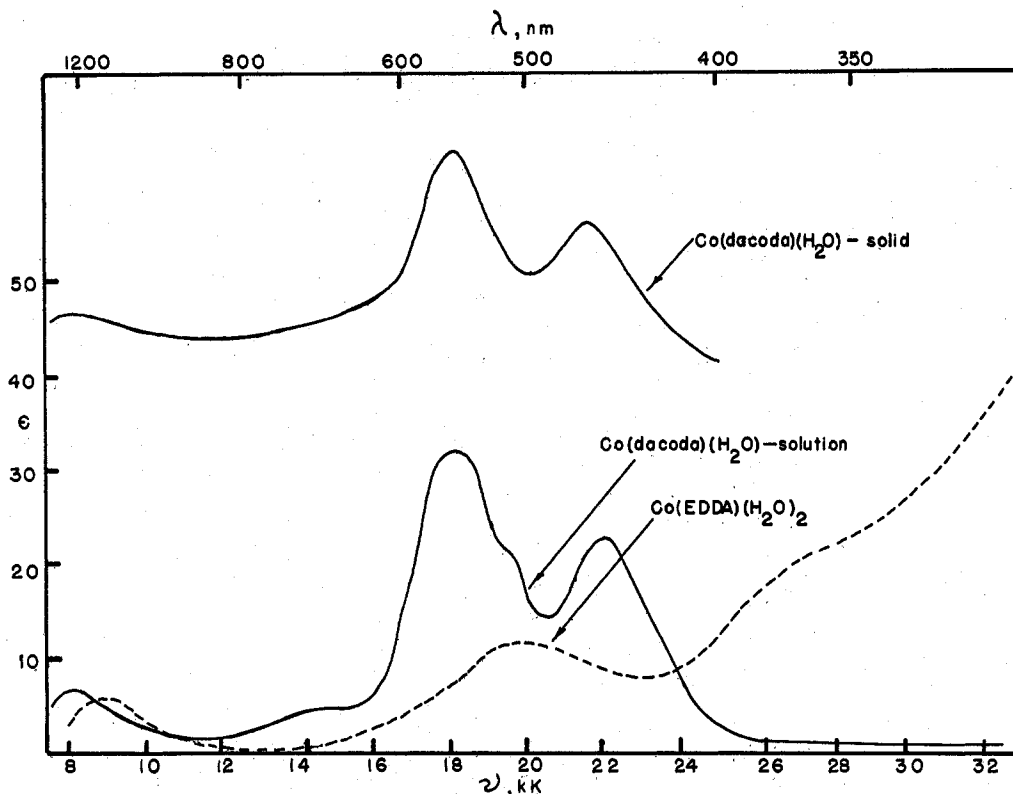

Figure 3.—The electronic absorption spectra of the cobalt(II) complexes. Relative absorbance is shown for the solid-state spectrum.

(H$_2$O)]·2H$_2$O were determined from room to liquid-nitrogen temperature. The corrected molar suscepti-bilities were calculated and their inverses plotted against temperature. The susceptibility followed the Curie–Weiss law, $\chi_{mc} = C/(T - \Theta)$, over the temper-ature range 77–300°K. From the plot of reciprocal molar susceptibility *vs.* temperature the values of C (slope is $1/C$) and Θ (Θ is T at intercept) were deter-mined. No attempt was made to give any significance to Θ other than its use in fitting the data. Table IV summarizes the data obtained. The effective mag-netic moment (μ_{eff}) is given at 77 and 293°K. The μ_{eff} shows only a small decrease (0.2 BM) in going from 293 to 77°K. The magnetic behavior of the complex is very much like that of octahedral com-plexes as has been found for other square-pyramidal high-spin Ni(II) complexes[16,17] and is not diagnostic of the five-coordinate geometry. It has been suggested that measurements of magnetic anisotropy may be of great value in distinguishing geometries since even regular five-coordinate complexes are expected to be anisotropic.[18]

(16) J. S. Judge and W. A. Baker, Jr., *Inorg. Chim. Acta*, **1**, 239 (1967).
(17) I. Bertini and F. Mani, *Inorg. Chem.*, **9**, 248 (1970); I. Bertini, D. L. Johnston, and W. DeW. Horrocks, Jr., *ibid.*, **9**, 698 (1970).
(18) D. J. Brown, M. Gerlock, and J. Lewis, *Nature (London)*, **220**, 256 (1968).

As would be expected the apical water on Ni(dacoda)-(H$_2$O) is easily lost to give the orange diamagnetic, square-planar complex. The spectrum of orange Ni-(dacoda) in nitromethane shows the expected single absorption corresponding to the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in D_{4h} (holohedrized approximation[15]) at 20.88 kK (ϵ 84.0 M^{-1} cm^{-1}). In comparison the stronger field Ni(daco)$_2$$^{2+}$ exhibits a band at 23.4 kK (ϵ 112) in nitro-methane.[6]

The Cobalt(II) Complexes.—The electronic absorp-tion spectrum of pink Co(EDDA)(H$_2$O)$_2$, Figure 3, is characteristic of those observed for Co(II) octahedral complexes.[19] The band assignments are given in Table II on the basis of O_h symmetry. The effective magnetic moment, 5.0 BM, is typical of octahedral cobalt(II) complexes.[11]

The violet dacoda–Co(II) complex exhibits a con-siderably different absorption spectrum, Figure 3. As was found for the corresponding Ni(II) complex, a greater molar absorptivity suggests the presence of a less symmetric field than is expected for the EDDA complex. A comparison of powder patterns, Table V, shows that [Co(dacoda)(H$_2$O)]·2H$_2$O is isomorphous with [Ni(dacoda)(H$_2$O)]·2H$_2$O, and comparison of the

(19) T. M. Dunn, D. S. McClure, and R. G. Pearson, "Some Aspects of Crystal Field Theory," Harper and Row, New York, N. Y., 1965.

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TABLE V

X-RAY POWDER PATTERN DATA FOR THE dacoda COMPLEXES[a]

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[Ni(dacoda)-(H₂O)]·2H₂O	[Co(dacoda)-(H₂O)]·2H₂O	[Zn(dacoda)-(H₂O)]·2H₂O	[Cu(dacoda)-(H₂O)]·2H₂O
1.23 s	1.22 s	1.21 vs	1.24 m
1.32 s	1.34 m	1.34 vs	1.34 w
1.38 vs	1.38 vs	1.43 vs	1.38 s
1.46 m	1.46 w	1.56 vw	1.48 vw
1.71 s	1.69 m	1.68 m	1.58 m
1.80 s	1.79 m	1.79 s	1.68 w
1.90 m	1.91 w	1.91 m	1.73 m
1.99 vw	2.03 w	1.98 w	1.78 w
2.09 s	2.08 m	2.09 s	1.82 w
2.20 w	2.21 vw	2.19 vw	1.90 vw
2.26 w		2.29 vw	1.99 s
2.33 w		2.35 vw	2.07 w
2.43 m		2.44 m	2.18 m
2.53 m	2.51 vw	2.52 m	
2.64 s	2.63 m	2.62 s	
2.76 m	2.75 w	2.76 s	

[a] 4θ values. Key: s, strong; v, very; m, medium; w, weak.

solid- and solution-state spectra of the Co(II) complex, Figure 3, establishes the square-pyramidal geometry in water. The solution- and solid-state ir spectra, Table III, show that the carboxylates are fully coordinated.

Although the degeneracy of the T states is removed in C_{4v} (or a lower symmetry) and a multiplicity of bands is observed in the spectrum of Co(dacoda)-(H₂O), nothing definitive can be said about state assignments in this case. In a study of square-pyramidal Co(II) complexes it was found that the magnetic moments became smaller and more temperature dependent as the symmetry was reduced.[20] The complex exhibited a temperature-dependent susceptibility similar to that observed for the corresponding Ni(II) complex. The pertinent data are summarized in Table IV. Again the magnetic data are not diagnostic of the five-coordinate geometry.

Perhaps the most interesting characteristic of Co-(dacoda)(H₂O) is its stability to oxidation. Unlike typical Co(II) amino acid like complexes, neither air nor hydrogen peroxide in the presence or absence of charcoal produces a Co(III) complex. Even attempts to synthesize a complex directly by substitution of Co(III) complexes yielded [Co(dacoda)(H₂O)]·2H₂O as the only easily identifiable complex. In contrast Co-(EDDA)(H₂O)₂ had to be prepared in the absence of air to ensure freedom from oxidized products. It might be argued that since Co(III) apparently forms only six-coordinate complexes in water, formation of the five-coordinate complex is excluded. However, dacoda may (also) kinetically inhibit the oxidation.

The Copper(II) Complexes.—The blue complexes of Cu(II) with EDDA and dacoda exhibit single, symmetric absorption bands in the red region, Table VI.

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TABLE VI

ELECTRONIC ABSORPTION SPECTRA OF THE Cu(II) AND RELATED COMPLEXES

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Complex	ν, kK	Complex	ν, kK
Cu(daco)₂²⁺ᵇ	19.95	Cu(EDDA)(H₂O)₂	14.9 (118ᵃ)
Cu(dacoda)(H₂O)	16.1 (152ᵃ)	Cu(EDTA)²⁻ᶜ	13.7
Cu(gly)₂(H₂O)₂ᶜ	15.8		

[a] Molar extinction coefficient, ϵ, M^{-1} cm^{-1}. [b] Reference 6. [c] C. K. Jørgensen, *Acta Chem. Scand.*, **9**, 1362 (1955).

The powder pattern of Cu(dacoda)·3H₂O, Table V, is significantly different from that of [Ni(dacoda)H₂O]·2H₂O and, consequently, does not support an isomorphous structure. However, there is little reason to doubt that Cu(dacoda)·3H₂O involves fully coordinated dacoda and is therefore five-coordinate. The infrared spectra, Table III, support full coordination of the acetates in both the solution and solid states. The magnetic moment of Cu(dacoda)·3H₂O varies only slightly with temperature (-0.07 BM in going from 293 to 77°K), Table IV. The lack of dependence of μ_{eff} on temperature and the value of μ_{eff} are typical of Cu(II) complexes which have no metal–metal interaction and support a mononuclear structure. The Cu(II)–EDDA complex exhibits a μ_{eff} of 1.76 BM.[21]

It is informative to examine the spectral change in going from Cu(daco)₂²⁺ to Cu(EDTA)²⁻ through Cu(dacoda)(H₂O), Cu(gly)₂(H₂O)₂, and Cu(EDDA)-(H₂O)₂ as summarized in Table VI. In principle the d–d transition(s) at 19.95 kK observed for Cu(daco)₂²⁺ can be assigned either to $xy \rightarrow x^2 - y^2$ or $z^2 \rightarrow x^2 - y^2$ depending upon the degree of axial perturbation. The latter choice facilitates an interpretation of the red shift shown in Table VI in going from Cu(daco)₂²⁺ to Cu(EDTA)²⁻ as follows. Cu(daco)₂²⁺ is most likely a good representative of a planar Cu²⁺ environment. As previously discussed the daco ligands should effectively block the axial positions, and this complex has been found to be relatively insensitive to the presence of good coordinating anions or solvents.[6] The band for Cu(dacoda)·H₂O is found at 16.1 kK. The decrease in energy can be attributed primarily to a lowering of the $x^2 - y^2$ orbital energy due to a decrease in the equatorial field (4 N's to 2 N's and 2 O's). In addition, the introduction of a water molecule into an axial position would raise the energy of the z^2 orbital. Structural information for the corresponding Ni(II) and Co(II) complexes shows that one axial site is effectively blocked by the dacoda backbone. In going from Cu(dacoda)·H₂O to Cu(gly)₂(H₂O)₂ under the reasonable assumption that the equatorial field remains the same, there should be no relative change in the position of the $x^2 - y^2$ orbital. Thus, the absorption band for Cu(gly)₂(H₂O)₂ should be shifted to lower energy and is found at 15.8 kK.

In the case of Cu(EDDA)(H₂O)₂ the chelate framework tends to constrain the acetate oxygens along the z^2 orbital; or, alternately, if the chelate is planar, the acetates would tend to be pulled away from the metal ion due to the expected strain in the framework analogous to that found for the in-plane acetates of Co(EDTA)⁻[22] and the energy of the $x^2 - y^2$ orbital would therefore be lowered. In either case lowering of the energy of the d–d transition would be expected and is found, Table VI. Finally, in the case of Cu(EDTA)²⁻ a similar situation for the trans acetates exists as is expected for *trans*-Cu(EDDA)(H₂O)₂ but the in-plane waters in Cu(EDDA)(H₂O)₂ have been replaced by two acetate oxygens which are probably not only pulled out from the metal ion due to ring strain but are weaker field ligands than water. Consequently, the energy of

(20) F. Lions, I. G. Dance, and J. Lewis, *J. Chem. Soc. A*, 565 (1967).

(21) The Cu complexes were recently determined to be monomeric in aqueous solution by molecular weight measurements. A Hitachi Perkin-Elmer 115 molecular weight apparatus calibrated against sucrose was used.
(22) H. A. Weakliem and J. L. Hoard, *J. Amer. Chem. Soc.*, **81**, 549 (1959).

the $x^2 - y^2$ orbital would be lowered and a lower energy transition would be expected and is found, Table VI.

The [Zn(dacoda)(H$_2$O)]·2H$_2$O Complex.—This complex is isomorphous with the corresponding Ni(II) complex as evidenced by the powder pattern, Table V, and there is little doubt that this structure is maintained in solution.

Electrochemical Investigation of Tris(2,2'-bipyridine) Complexes of Chromium(III)

BY DONALD M. SOIGNET[*2a] AND LARRY G. HARGIS[2b]

Tris(2,2'-bipyridine)chromium(III) undergoes a one-electron reduction at −0.50 V followed by a series of reactions which converts all unreduced tris(2,2'-bipyridine)chromium(III) to diaquobis(2,2'-bipyridine)chromium(III) and free 2,2'-bipyridine. The diaquobis(2,2'-bipyridine)chromium(III) complex can be reduced to the corresponding chromium(II) complex. In the presence of excess 2,2'-bipyridine, the diaquobis(2,2'-bipyridine)chromium(II) forms the tris(2,2'-bipyridine)chromium(II) complex by ligand exchange. In the absence of excess 2,2'-bipyridine, the final products are equimolar quantities of the tris(2,2'-bipyridine)chromium(II) and the tetraaquo(2,2'-bipyridine)chromium(II) complexes.
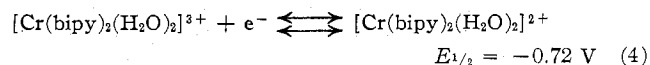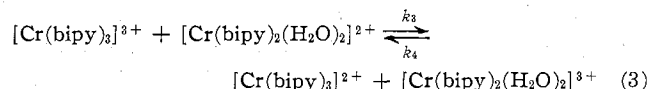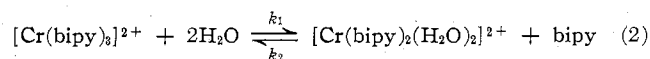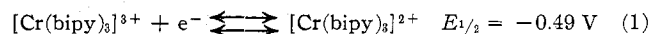
Introduction

The tris(2,2'-bipyridine)chromium(III) ion has been the subject of several electrochemical studies. In aprotic solvents, such as acetonitrile, the tris complex apparently reduces in four well-defined, one-electron steps to the $[Cr(bipy)_3]^-$ anion.[3] The electrochemistry of this ion in water, however, is not simple or well understood and there is still considerable lack of agreement among investigators of this system.

Using a commutator technique to obtain current–voltage curves, Vlcek[4] reported three polarographic waves ($E_{1/2}$ *vs.* sce of −0.36, −0.73, and −1.38 V) for the tris(2,2'-bipyridine)chromium(III) ion in aqueous 0.5 *M* sodium chloride supporting electrolyte. By comparison of the wave heights with those for the hexaamminechromium(III) ion, Vlcek concluded that each of the waves corresponded to a reversible one-electron transfer, resulting finally in a tris(2,2'-bipyridine)chromium(0) complex. Vlcek reported no evidence of dissociation of the complex during any stage of the reduction.

Using conventional polarographic techniques Baker and Dev Mehta[5] and Tucker, *et al.*,[6] obtained four polarographic waves with half-wave potentials that were substantially different from those obtained by

Vlcek. From the behavior of the first two polarographic waves with regard to temperature and pH, Baker and Dev Mehta[5] suggested the mechanism shown below whereby the $[Cr(bipy)_3]^{3+}$ underwent catalytic ligand exchange at the dme surface to $[Cr(bipy)_2(H_2O)_2]^{3+}$ which reduced more cathodically than the tris complex.

In the following equations the symbol $\rightleftarrows$ represents polarographically reversible reaction at the half-wave potential indicated

$$[Cr(bipy)_3]^{3+} + e^- \rightleftarrows [Cr(bipy)_3]^{2+} \quad E_{1/2} = -0.49 \text{ V} \quad (1)$$

$$[Cr(bipy)_3]^{2+} + 2H_2O \underset{k_2}{\overset{k_1}{\rightleftarrows}} [Cr(bipy)_2(H_2O)_2]^{2+} + \text{bipy} \quad (2)$$

$$[Cr(bipy)_3]^{3+} + [Cr(bipy)_2(H_2O)_2]^{2+} \underset{k_4}{\overset{k_3}{\rightleftarrows}}$$
$$[Cr(bipy)_3]^{2+} + [Cr(bipy)_2(H_2O)_2]^{3+} \quad (3)$$

$$[Cr(bipy)_2(H_2O)_2]^{3+} + e^- \rightleftarrows [Cr(bipy)_2(H_2O)_2]^{2+}$$
$$E_{1/2} = -0.72 \text{ V} \quad (4)$$

Although Baker and Dev Mehta did investigate the reduction of $[Cr(bipy)_3]^{3+}$, they did not report on the further reduction of the resulting chromium(II) species. This paper presents a detailed study of the entire system, namely, $[Cr(bipy)_3]^{3+}$, $[Cr(bipy)_2(H_2O)_2]^{3+}$ + bipyridine, and $[Cr(bipy)_2(H_2O)_2]^{3+}$, using polarographic, controlled-potential electrolysis, and cyclic voltammetric techniques. Cyclic voltammetry is particularly well suited to studying chemical reactions following an electron transfer[7,8] and we found it very useful in helping to characterize the systems studied here. In addition, several interesting observations are

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