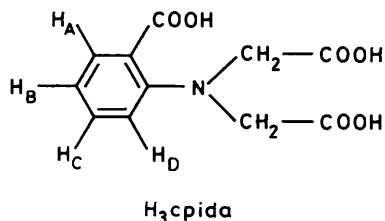


Synthesis and Spectral Characterization of Cobalt(III) Complexes of *N*-(*o*-Carboxyphenyl)iminodiacetic acid†

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The complexes $[\text{Co}(\text{cpida})(\text{N-N})] \cdot n\text{H}_2\text{O}$ [$\text{H}_3\text{cpida} = N$ -(*o*-carboxyphenyl)iminodiacetic acid, N-N = ethylenediamine, 1,2-diaminopropane, or 1,3-diaminopropane] have been synthesized from $\text{trans}-[\text{Co}(\text{N-N})_2\text{Cl}_2]^+$ as well as by direct oxidation procedures. The dinitro complex $\text{Na}_2[\text{Co}(\text{cpida})(\text{NO}_2)_2]$ has been synthesized from $\text{Na}_3[\text{Co}(\text{NO}_2)_4(\text{CO}_3)]$. They have been characterized by u.v.-visible, i.r., and ^1H n.m.r. spectroscopy. The amine spectral pattern and the acetate splitting in the ^1H n.m.r. offers valuable information about the geometry of the ligand around the metal ion.

Extensive studies have been carried out on Co^{III} complexes of linear quadridentate amino polycarboxylic acid ligands.^{1,2} In marked contrast, complexes with tripod-type ligands such as nitrilotriacetic acid (H_3nta) or *N*-(*o*-carboxyphenyl)iminodiacetic acid (H_3cpida) have been little studied.³ Several mixed-ligand Cr^{III} complexes with cpida^{3-} have been reported^{4,5} but their Co^{III} analogues are as yet unreported. Although Kauzman Anton *et al.*⁶ reported the formation of a Co^{III} - cpida complex in solution by oxidizing Co^{II} and H_3cpida with hydrogen peroxide, no attempt was made to isolate it in the solid state. The $[\text{Co}(\text{cpida})(\text{H}_2\text{O})_2]$ thus formed is unstable towards reduction and turns yellow



on standing. More stable complexes containing diamine and nitro ligands have now been synthesized for the first time. The presence of an aromatic group in one of the legs of the tripod reduces the possibility of obtaining geometrical isomers. Characterization by various spectroscopic techniques and a detailed study of the ^1H n.m.r. spectra were carried out to gain insight into the structures of the complexes.

Experimental

Synthesis of the Ligand.—*N*-(*o*-Carboxyphenyl)iminodiacetic acid (H_3cpida) was prepared according to the reported procedure.⁷

Synthesis of the Complexes.— $[\text{Co}(\text{cpida})(\text{en})] \cdot 2\text{H}_2\text{O}$. (a) **Direct oxidation.** A mixture of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.005 mol, 1.15 g), H_3cpida (0.005 mol, 1.27 g), ethylenediamine (en) (0.0067 mol, 0.45 g), and activated charcoal (0.3 g) in water (40 cm^3) was air oxidized for 4 h at room temperature. After removing the charcoal the filtrate was concentrated to ca. 10–15 cm^3 and kept in a refrigerator overnight. The resulting violet crystals were recrystallized from the minimum amount of water, washed with water and ethanol, and air dried. Yield: 1.62 g, 80%

(Found: C, 38.20; H, 4.80; N, 10.30. $\text{C}_{13}\text{H}_{16}\text{CoN}_3\text{O}_6 \cdot 2\text{H}_2\text{O}$ requires C, 38.50; H, 4.95; N, 10.35%).

(b) **Substitution.** $\text{trans}-[\text{Co}(\text{en})_2\text{Cl}_2]^+$ (0.005 mol, 1.43 g) and H_3cpida (0.005 mol, 1.27 g) were dissolved in water (50 cm^3). After raising the pH of the solution to 6–7 by sodium hydroxide, it was heated on a steam-bath until crystals started to appear. Cooling to room temperature separated the crude product containing violet and yellow crystals. The more soluble yellow crystals were separated from the violet crystals $[\text{Co}(\text{cpida})(\text{en})] \cdot 2\text{H}_2\text{O}$ by repeated washing with cold water. Yield: 1.42 g, 70%. Evaporation of the initial washing to a small volume yielded yellow crystals which were identified as $[\text{Co}(\text{en})_3]\text{Cl}_3$ on the basis of u.v.-visible data.⁸

The other diamine complexes $[\text{Co}(\text{cpida})(\text{N-N})] \cdot 3\text{H}_2\text{O}$ [N-N = 1,2-diaminopropane (pn) or 1,3-diaminopropane (pd)] were prepared, by both methods, in an identical manner. Yield: 1.64 g, 75% and 1.53 g, 70%, respectively {Found for $[\text{Co}(\text{cpida})(\text{pn})] \cdot 3\text{H}_2\text{O}$: C, 38.10; H, 5.60; N, 9.50. $\text{C}_{14}\text{H}_{18}\text{CoN}_3\text{O}_6 \cdot 3\text{H}_2\text{O}$ requires C, 38.45; H, 5.50; N, 9.60. Found for $[\text{Co}(\text{cpida})(\text{pd})] \cdot 3\text{H}_2\text{O}$: C, 38.60; H, 5.45; N, 9.70. $\text{C}_{14}\text{H}_{18}\text{CoN}_3\text{O}_6 \cdot 3\text{H}_2\text{O}$ requires C, 38.45; H, 5.50; N, 9.60%}.

$\text{Na}_2[\text{Co}(\text{cpida})(\text{NO}_2)_2]$. $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ (0.005 mol, 2 g) and anhydrous sodium carbonate (0.005 mol, 0.53 g) were added to water (5 cm^3) and the reaction mixture stirred thoroughly until the solution changed from brownish yellow to red, resulting in the formation of $\text{Na}_3[\text{Co}(\text{NO}_2)_4(\text{CO}_3)]$. H_3cpida (0.005 mol, 1.27 g) was added in small portions and stirred until effervescence ceased. Ethanol (20 cm^3) was added to the ice-cold reaction mixture with constant stirring to obtain a red coloured substance. The mother-liquor was decanted off and ethanol (50 cm^3 , in portions) added until a red solid separated out. The solid was washed with an ice-cold ethanol-water (2:1) mixture and absolute ethanol and finally dried over vacuum to yield $\text{Na}_2[\text{Co}(\text{cpida})(\text{NO}_2)_2]$. Yield: 1.34 g, 60% (Found: C, 29.20; H, 1.90; N, 9.45. $\text{C}_{11}\text{H}_8\text{CoNa}_2\text{N}_3\text{O}_{10}$ requires C, 29.50; H, 1.70; N, 9.40%).

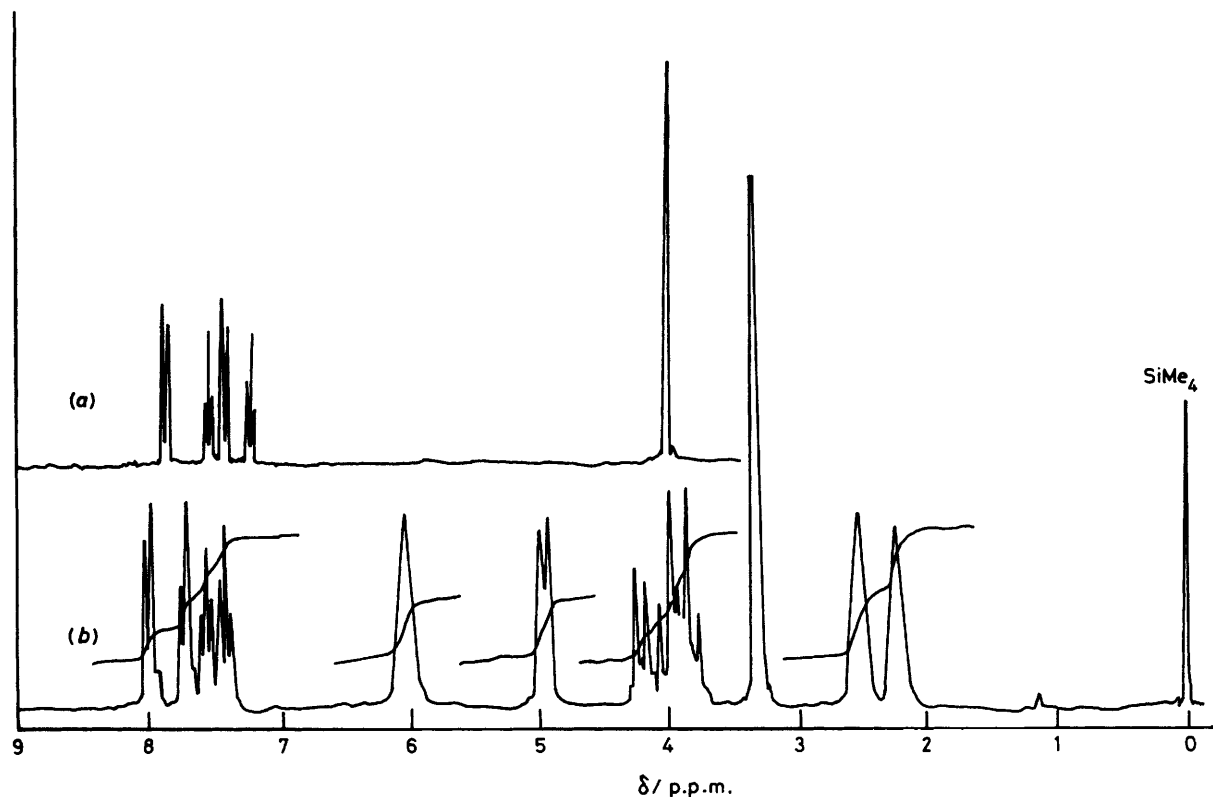
$\text{trans}-[\text{Co}(\text{N-N})_2\text{Cl}_2]^+$ (N-N = en, pn, or pd) and $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ were prepared according to published procedures.^{9–11} The purity of the complexes was ascertained by spectral analysis.

Apparatus.—U.v.-visible spectra were recorded on a Shimadzu UV 260 spectrophotometer and i.r. spectra in KBr on a Nicolet 170 SX spectrophotometer. ^1H n.m.r. spectra were run on Varian XL-100 and 200 MHz spectrometers. Homonuclear spin-decoupling experiments were carried out on a Bruker 500 MHz spectrometer. Thermogravimetric analyses were carried out on a Dupont thermal balance with a heating range of 5 $^\circ\text{C min}^{-1}$ in a nitrogen atmosphere. Conductivity measurements were made on Toshniwal digital conductivity

† Non-S.I. unit employed: $\text{eV} \approx 1.60 \times 10^{-19}$ J.

Table 1. Electronic spectral data

Complex	Band					
	I		II		III	
	$10^{-3}\bar{\nu}/\text{cm}^{-1}$	$\log \epsilon$	$10^{-3}\bar{\nu}/\text{cm}^{-1}$	$\log \epsilon$	$10^{-3}\bar{\nu}/\text{cm}^{-1}$	$\log \epsilon$
[Co(cpida)(en)]·2H ₂ O	19.34	2.17	27.77	2.21(sh)	45.45	4.38
[Co(cpida)(pn)]·3H ₂ O	19.34	2.18	27.62	2.25(sh)	45.04	4.39
[Co(cpida)(pd)]·3H ₂ O	19.15	2.18	27.77	2.28(sh)	44.20	4.38
Na ₂ [Co(cpida)(NO ₂) ₂]	19.68	2.18	28.57	2.46(sh)	39.06	3.96

Figure. ¹H N.m.r. spectra of (a) H₃cpida in (CD₃)₂SO and (b) [Co(cpida)(en)]·2H₂O in (CD₃)₂SO

meter. X-Ray photoelectron spectra were recorded on a VG Scientific ESCA-3 Mark II spectrometer using Al-K_α as a radiation source.

Results and Discussion

Akamatsu *et al.*³ have reported the preparation of [Co(NTA)(N-N)] (N-N = en or pn, H₃nta = nitrilotriacetic acid) involving the substitution of labile groups in *cis*-[Co(N-N)(NH₃)₂Cl₂]⁺ by nta³⁻. This method suffers from an inherent disadvantage however as the synthesis of the precursor complex *cis*-[Co(N-N)(NH₃)₂Cl₂]⁺ involves several steps. A more direct synthesis has been developed involving the reaction of *trans*-[Co(N-N)₂Cl₂]⁺ with H₃cpida at pH ≈ 6 to yield [Co(cpida)(N-N)]. This reaction is of particular importance since it is known that the diamine moiety is kinetically inert and is retained even under drastic acidic and basic conditions. However in the presence of the quadridentate ligand the robust diamine moiety is replaced under milder pH conditions, a manifestation of the multidentate effect offered by an amino polycarboxylate ion.

Electronic Spectra.—The absorption spectra of the series of complexes examined here (Table 1) showed two bands at *ca.* 19.23 × 10³ and 27.77 × 10³ cm⁻¹ which are assigned to ¹A_{2g} → ¹T_{2g} and ¹A_{1g} → ¹T_{2g} transitions respectively. The positions of the bands are similar to those observed for analogous *mer*-Co^{III}N₃O₃ systems.³

I.r. Spectra.—All the complexes showed strong absorptions in the region 1 648—1 658 cm⁻¹, characteristic of co-ordinated carboxyl groups. The amine complexes showed a doublet in the region 3 000—3 300 cm⁻¹ for the primary amine group while the dinitro complex Na₂[Co(cpida)(NO₂)₂] exhibited frequencies for the co-ordinated nitro groups at 623—627, 825—840, 1 330—1 335, and 1 400—1 425 cm⁻¹.¹² The metal—nitrogen and metal—oxygen stretching frequencies occur in the ranges 400—500 and 300—400 cm⁻¹ respectively for all complexes reported here.

Conductivity Measurements.—The molar conductivities of the diamine complexes lie in the range 0—6 S cm² mol⁻¹

Table 2. ^1H N.m.r. assignments^a

(a) H_3cpida			
Aromatic protons	H_A , 7.85(d); H_B , 7.20(dd)		
	H_C , 7.53(dd); H_D , 7.40(d)		
	$(J_{AB} 7.57, J_{BC} 7.11, J_{CD} 8.2 \text{ Hz})$		
Acetate protons	H_E 4.0 ^b		
(b) Complexes			
	$>\text{N}-\text{CH}_2\text{COO}^-$ (R ring)	$>\text{N}-\text{CH}_2\text{COO}^-$ (G ring)	$-\text{NH}_2$
$[\text{Co}(\text{cpida})(\text{en})]\cdot 2\text{H}_2\text{O}$	4.32, 4.16, 3.96, 3.72	4.02	6.04, 5.1, 4.94
$[\text{Co}(\text{cpida})(\text{pn})]\cdot 3\text{H}_2\text{O}$	4.30, 4.16, 3.94, 3.74	4.02	6.30, 5.60, 5.06
$[\text{Co}(\text{cpida})(\text{pd})]\cdot 3\text{H}_2\text{O}$	4.30, 4.16, 3.90, 3.72	4.02	5.86, 5.12, 4.04 ^c
$\text{Na}_2[\text{Co}(\text{cpida})(\text{NO}_2)_2]$	4.32, 4.16, 3.96, 3.72	4.02	

^a All chemical shifts are relative to SiMe_4 and expressed in p.p.m.

^b Sharp singlet. ^c Overlapping with acetate G ring.

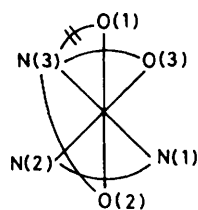
indicating that they are neutral complexes while the dinitro complex has a value of $160 \text{ S cm}^2 \text{ mol}^{-1}$, corresponding to a 1:2 electrolyte.

Thermogravimetric Analysis.—The thermogravimetric analysis showed that loss of water of crystallization occurs in the range 70–140 °C and the complexes decomposed around 250–300 °C.

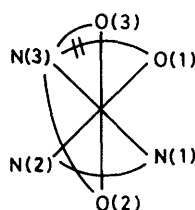
X-Ray Photoelectron Spectra.—The 1s nitrogen photoelectron spectrum of $\text{Na}_2[\text{Co}(\text{cpida})(\text{NO}_2)_2]$ shows two peaks at binding energies 400.2 and 403.7 eV with a relative intensity of 1:2, assignable to the tertiary nitrogen of cpida and NO_2^- respectively. Only one peak with a binding energy of 399.3 eV was observed in the case of $[\text{Co}(\text{cpida})(\text{en})]\cdot 2\text{H}_2\text{O}$.

Proton N.M.R.—*The ligand.* The H_3cpida ligand possess four aromatic (H_A , H_B , H_C , H_D) and four acetate (H_E) CH_2 protons. The ^1H n.m.r. spectrum in $(\text{CD}_3)_2\text{SO}$ [Figure (a)] shows the aromatic protons in the region 7–8 p.p.m. and the acetate protons as a sharp singlet at 4.0 p.p.m. The *ortho* (H_A) and *para* (H_C) protons experience the deshielding effect of the carboxyl group and hence appear downfield with respect to the H_B and H_D protons. Chemical shifts and coupling constants are summarized in Table 2.

$[\text{Co}(\text{cpida})(\text{en})]\cdot 2\text{H}_2\text{O}$. The ^1H n.m.r. spectrum of $[\text{Co}(\text{cpida})(\text{en})]\cdot 2\text{H}_2\text{O}$ [Figure (b)] is discussed as a representative example of diamine cpida complexes. The aromatic protons experience a downfield shift on complexation, the maximum being felt by the H_D proton. The amine protons of ethylenediamine appear as broad resonances at 6.04, 5.1, and 4.94 p.p.m. with an intensity ratio of 2:1:1. Extending Freeman's rule¹³ as applied to amino polycarboxylate complexes the resonance at 6.04 p.p.m. is assigned to the amine protons *trans* to N(3)



(I)



(II)

whereas the signals at 5.1 and 4.94 p.p.m. are assigned to the protons *trans* to O(3) [see (I) below]. The splitting of the upfield amine signal is ascribed to the anisotropic effect of the aromatic rings as no such splitting is observed for analogues complexes of nta^{3-} and nitrilodiacetatepropionate.¹⁴ The acetate protons undergo splitting on complexation due to the restricted rotation making them non-equivalent. An AB pattern originates from protons on the R ring (out-of-plane ring) while a sharp singlet is observed for protons on the G ring (in-plane ring).¹⁵ In the title complex, there are two acetate arms and hence two configurations, (I) and (II), are possible, where N–H–O defines the phenylcarboxylate arm. The observed AB pattern at 4.32, 4.16, 3.96, 3.72 p.p.m. (J 16–18 Hz) and a sharp singlet at 4.02 p.p.m. suggests the presence of both R and G type rings, as required for (I) and hence this structure is assigned for the complex.

The methylene protons of ethylenediamine appear as two broad peaks at 2.60 and 2.30 p.p.m. with relative intensity 2:2. The non-equivalence is suggested to arise from the different average fields which the pairs of protons experience. The aromatic and acetate splitting patterns are almost identical in the other complexes. The amines and the acetate chemical shifts are summarized in Table 2.

The ^1H n.m.r. of $[\text{Co}(\text{cpida})(\text{pn})]\cdot 3\text{H}_2\text{O}$ prepared by the direct oxidation procedure revealed two methyl doublets at 1.35 and 1.08 p.p.m. indicating that the complex is a mixture of two isomers *trans*- N_iN^* and *cis*- N_iN^* , where N_i is the tertiary nitrogen on cpida and N^* is the nitrogen adjacent to the asymmetric carbon of pn. A similar observation was made in the ^1H n.m.r. of $[\text{Co}(\text{nta})(\text{pn})]$, but the methyl resonances were not assigned to the corresponding isomers. The methyl doublet at 1.35 p.p.m. is assigned to the *trans*- N_iN^* isomer while the doublet at 1.08 p.p.m. is assigned to the *cis*- N_iN^* isomer based on Freeman's¹³ arguments. However, the *trans*- N_iN^* isomer was predominantly obtained by the substitution method.

A striking feature in the ^1H n.m.r. spectrum of $[\text{Co}(\text{cpida})(\text{pd})]\cdot 3\text{H}_2\text{O}$ is the reversal in intensity of the methylene proton resonances of 1,3-diaminopropane (pd). The methylene protons resonate at 2.80 and 1.80 p.p.m. with an intensity ratio 2:4. A similar type of reversal in intensity as compared to the free ligand was observed in *cis*- $[\text{Co}(\text{pd})_2(\text{H}_2\text{O})(\text{HPO}_4)]^+$,¹⁰ *cis*- $[\text{Co}(\text{pd})_2(\text{H}_2\text{O})_2]^{3+}$,¹⁰ and *cis*- $[\text{Co}(\text{pd})_2(\text{CN})_2]^+$.¹⁶ The above feature indicates that the $\alpha\text{-CH}_2$ protons become magnetically non-equivalent. It is proposed that in $[\text{Co}(\text{cpida})(\text{pd})]\cdot 3\text{H}_2\text{O}$, the downfield peak can be ascribed to the $\alpha\text{-CH}_2$ protons adjacent to the amine *trans* to the tertiary nitrogen whereas the upfield signal is due to overlap of $\alpha\text{-CH}_2$ protons adjacent to the amine *trans* to the oxygen and the $\beta\text{-CH}_2$ protons. The non-equivalence of the acetate and amines is reflected in the metal–nitrogen and metal–carboxylate bond lengths. The X-ray crystal analysis of the complex $[\text{Co}(\text{cpida})(\text{pd})]\cdot 3\text{H}_2\text{O}$ ¹⁷ revealed that cpida³⁻ co-ordinates through its tertiary nitrogen N(3), carboxylic oxygen O(1), and carboxylate oxygens O(2) and O(3). The diamine co-ordinates through nitrogen N(1) and N(2) as in (I). The Co–N(1) and Co–N(2) bond lengths were found to be 1.924(4) and 1.951(4) Å respectively. The Co–O(2) and Co–O(3) bond lengths were found to be 1.915(4) and 1.858(2) Å which are consistent with the observed metal–oxygen bond lengths for out-of-plane acetate (1.915 Å) and in-plane (1.885 Å) rings.¹⁸ Hence the assignment of acetate rings from ^1H n.m.r. data is in agreement with the X-ray analysis. The Co^{III} -pd ring did not show any special twist and has a chair configuration.

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