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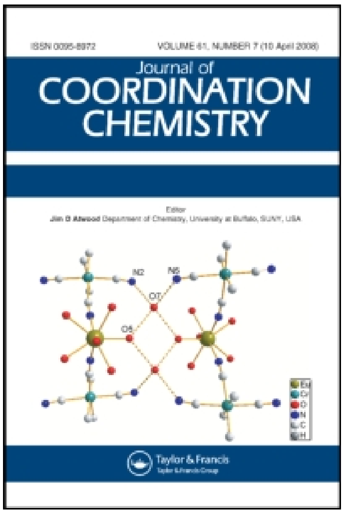

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A CARBON-13 NMR STUDY OF *POLAR*-(NITRO)TRIMETHYLENEDIAMINE-*N,N,N'*-TRIACETATOCOBALTATE(III) ION

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A CARBON-13 NMR STUDY OF *POLAR*-(NITRO)TRIMETHYLENEDIAMINE-*N,N,N'*-TRIACETATOCOBALTATE(III) ION

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The complex ion $[Co(1,3\text{-pd3a})NO_2]^-$ (pd3a = trimethylenediamine-*N,N,N'*-triacetate ion) was prepared from *equatorial-skew*-$[Co(1,3\text{-pd3a})H_2O]$. The absorption spectrum and the ^{13}C NMR spectrum show the nitro product to be a polar isomer. The diamine backbone ring is believed to have the chair conformation.

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INTRODUCTION

The applications of ^{13}C nuclear magnetic resonance (NMR) to the study of the stereochemistry of diamagnetic cobalt(III) complexes is rather new.[1-9] Carbon-13 NMR studies of cobalt(III) complexes of ethylenediamine-*N,N,N',N'*-tetraacetate (edta) type ligands,[10,11] phenyl substituted edta type ligands,[10,12] and ethylenediamine-*N,N,N'*-triacetate (ed3a) type ligands[10,13] have been reported recently. The equatorial and axial methyl substituent effects observed by substituting a methyl group for the equatorial hydrogen at the backbone terminal carbon have been rationalized by spectral comparison and using simple organic molecules as models. The strain in $[Co(edta)]^-$ is relieved by removal of one of the two strained equatorial glycinate arms (to give [Co(ed3a)X]) or by changing the 5-membered backbone diamine ring to a 6-membered diamine ring (to give $[Co(1,3\text{-pdta})]^-$ where 1,3-pdta = trimethylenediamine *N,N,N',N'*-tetraacetate ion). The degree of strain relief seems to be greater for $[Co(1,3\text{-pdta})]^-$ than for [Co(ed3a)X]. In order to evaluate the combination of the strain-relief effects in a complex of a quinquedentate ligand with a 6-membered diamine backbone ring, two complexes [Co(1,3-pd3a)X] were synthesized, where 1,3-pd3a = trimethylenediamine-*N,N,N'*-triacetate ion and X = NO_2^- or H_2O.

EXPERIMENTAL PROCEDURE

The free ligand, 1,3-pd3a, and the aqua complex were prepared by the published method,[14] 1,3-pd3a was abbreviated as trdtra in reference 14. The nitro complex was prepared by mixing the aqua complex with an equimolar amount of KNO_2 in aqueous solution.[15,16] Both complexes were purified by passing aqueous solutions through a column packed with a cation exchange resin (Dowex 50W-1X, 100–200 mesh) in the H^+ form and by recrystallization. The complexes were characterized by their distinctive absorption spectra in the visible region.[14,16] (Figure 1).

The ^{13}C NMR spectra were obtained as described previously.[11-13]

RESULTS AND DISCUSSION

The absorption spectrum of the purple aqua complex (Figure 1) shows splitting in the low energy band region, indicating low effective symmetry. The spectrum agrees with that reported[14] for *eq-skew*-$[Co(1,3\text{-pd3a})H_2O]$.

The replacement of H_2O by NO_2^- in *eq-skew*-$[Co(1,3\text{-pd3a})H_2O]$ was expected to produce *eq-skew*-$[Co(1,3\text{-pd3a})NO_2]^-$. However, the absorption spectrum of the red product (Figure 1) has one sharp maximum at 505 nm and a characteristic intense charge-transfer band below 400 nm which obscures completely the second *d–d* band. The absence of splitting of the 505 nm band indicates high symmetry which is inconsistent with an equatorial isomer, but is expected for a polar isomer (Figure 2). Doh *et al.* prepared [Co(1,3-pd3a)X] complexes where X is H_2O, NH_3, Cl^-, and CN^-, but not NO_2^-. Nevertheless, NO_2^- and CN^- are both strong field ligands and the very sharp band observed (Figure 1) for the NO_2^-

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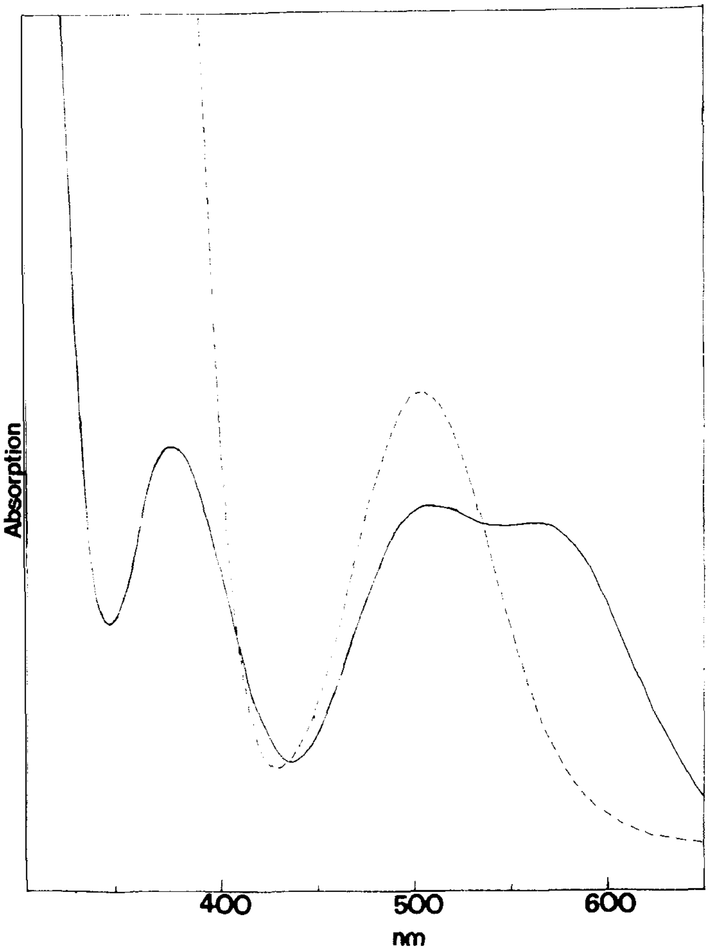

FIGURE 1 Absorption spectra of *eq-skew*-[Co(1,3-pd3a)H_2O] (———) and *polar-chair*-[Co(1,3-pd3a)NO_2]$^-$ (– – – –) (relative absorption scale).

complex is very similar to that reported[14] for *polar-chair*-[Co(1,3-pd3a)CN]$^-$, a red complex. In fact with cyanide ion Doh *et al.* were able to obtain the *polar-chair*-isomer. In the other cases they were able to obtain the *polar-skew* and *equatorial-skew* isomers as well. The similarity between CN^- and NO_2^- as ligands should lead one to expect the *eq-skew* → *polar* isomerization observed here on substitution of NO_2^- for H_2O.

The 60 MHz NMR spectra were recorded for both complexes. The ^{13}C NMR spectrum was obtained only for the nitro complex because of the low solubility in water of the uncharged [Co(1,3-pd3a)H_2O]. Figure 2 lists the structures of [Co(1,3-pd3a)NO_2]$^-$ and related complexes. The removal of one in-plane acetate arm of [Co(1,3-pdta)]$^-$ to form *eq*-[Co(1,3-pd3a)NO_2]$^-$ would leave all carbons nonequivalent so one would expect 9 ^{13}C peaks. For the polar isomer the two in-plane glycinate rings are very similar, although the carbons b and b′ differ in being attached to tertiary and secondary amine nitrogens, respectively. The observation of only two peaks in the carbonyl region (182.21 and 184.03 ppm) is consistent with the assignment as a polar isomer with the two in-plane carbonyl carbons equivalent. The more intense peak at 182.21 ppm is assigned to the *a* carbons, while that at 184.03 ppm is assigned to *f*. Selective decoupling experiments distinguish the glycinate methylenes (*b*, *b*′ and *e*) from the backbone methylenes (*c*, *c*′ and *d*). The remaining assignments in Table I and Figure 3 were made from these results and comparisons to similar complexes.

The chemical shift for the *b* carbon is similar to

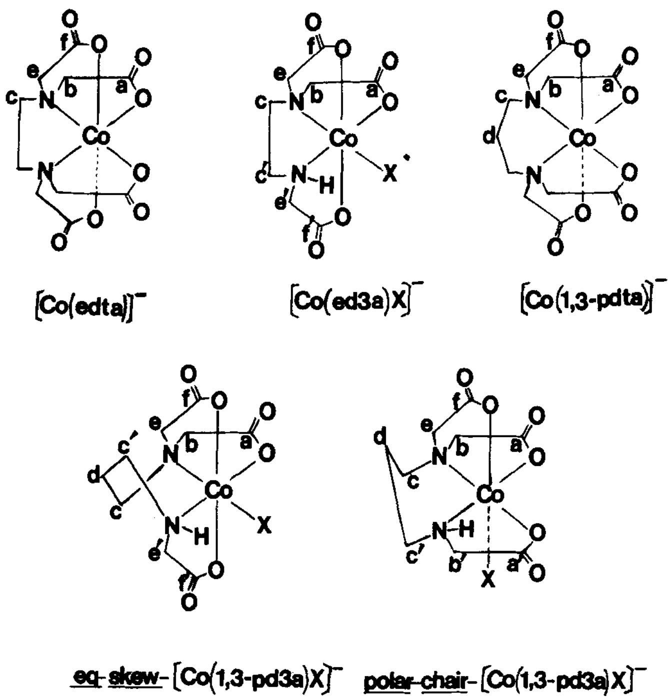

FIGURE 2 Designations of carbon atoms in structures of interest.

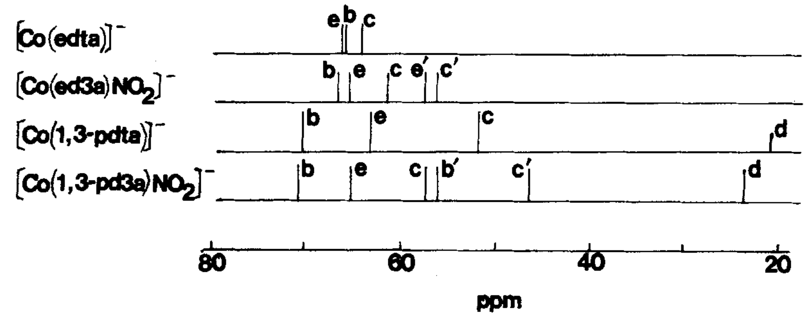

FIGURE 3 Stick diagram of the ^{13}C NMR spectra in the methylene region for *polar-chair*-[Co(1,3-pd3a)NO_2]$^-$ and related complexes.

TABLE I
^{13}C Chemical shift data of some complexes of interest[a]

Compound	Designation *a*	*a'*	*b*	*b'*	*c*	*c'*	*d*	*e*	*e'*	*f*	*f'*
[Co(edta)]$^{-b}$	182.4		65.77		64.00			66.00		183.0	
cis-eq-[Co(ed3a)NO_2]$^{-b}$	182.62		66.48		61.12	56.09		65.18	57.22	184.09	186.09
[Co(1,3-pdta)]$^{-b}$	181.84		70.35		52.03		21.49	63.21		183.66	
polar-chair-[Co(1,3-pd3a)-NO_2]$^-$	182.21	182.21	70.76	56.30	57.22	46.54	24.01	65.16	–	184.03	

[a] Positive sign indicates a downfield shift from TMS.
[b] Data are taken from Ref. 11.

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that for $[Co(1,3\text{-pdta})]^-$. The chemical shifts for the backbone carbons (*c*, *c*′, and *d*) differ considerably from those of $[Co(1,3\text{-pdta})]^-$, suggesting a different conformation of the backbone ring for $[Co(1,3\text{-pd3a})NO_2]^-$, as might be expected as a result of the relief of strain caused by removal of one acetate ring. The backbone of $[Co(1,3\text{-pdta})]^-$ has the skew-boat conformation. The shift observed for carbon *e* is closer to that observed for *cis-eq*-$[Co(ed3a)NO_2]^-$ than for $[Co(1,3\text{-pdta})]^-$, in agreement with the change in conformation of the diamine backbone. Doh *et al.* assigned the only isomer of $[Co(1,3\text{-pd3a})CN]^-$ as polar-chair, in agreement with the conformational change from *skew*-$[Co(1,3\text{-pdta})]^-$ observed here.

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