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The Configuration of the Cations Dinitrobis(1,10-phenanthroline)cobalt(III) and Dinitrobis(2,2′-bipyridyl)cobalt(III)

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A preparative study has been made of the compounds of the cations $[Co(phen)_2(NO_2)_2]^+$ *and* $[Co(bipy)_2(NO_2)_2]^+$ *(where phen = 1,10-phenanthroline and bipy = 2,2′-bipyridyl) to check previously conflicting claims about the configurations of these cations. The compounds were made by a variety of routes; but, although different crystalline species of some of the compounds now have been recognised, there is evidence for only one isomer of each cation. That this has the cis configuration is proven by the* ^1H *n.m.r. spectra. No evidence could be obtained for trans or for nitrito isomers. The "second stage" previously observed in the acid hydrolysis of* $[Co(bipy)_2(NO_2)_2]^+$ *is shown to involve disproportionation to the tris-bipyridyl species. The* ^1H *n.m.r. spectra in DMSO of various salts of these bis-chelated cations with different anions show differences which are interpreted as evidence for geometrically specific ion-pairs.*

Introduction

There is no unequivocal evidence for a *trans* octahedral configuration in bis(2,2′-bipyridyl) and bis(1,10-phenanthroline) metal compounds;[1] although several earlier assignments of this configuration appear to be worthy of further investigation.

One such is the problem of the configuration of the cations $[Co(bipy)_2(NO_2)_2]^+$ and $[Co(phen)_2(NO_2)_2]^+$ for which various methods of preparation have been described.[2–5] Ablov[2] first reported $[Co(phen)_2(NO_2)_2]NO_3 \cdot 2H_2O$ and assigned a *cis* configuration without proof. Later preparations,[3,4] by a method which had been demonstrated to give *trans*-$[Co(en)_2(NO_2)_2]^+$, were assumed to give *trans* isomers of both the bipy and phen cations. Lambert and Mason[3] did record their doubts, noting the similarity of their product to Ablov's; but Gomwalk and McAuley[4] observed a two-stage reaction for the acid hydrolysis of $[Co(bipy)_2(NO_2)_2]^+$, and interpreted this in terms of an initial *trans* species isomerising to a *cis* species. Palade *et al.*[5] described a different preparation of the bipy cation, and assigned a *cis* configuration – again without proof.

We have now prepared the various compounds by the published methods, and some new ones, and show, from their ^1H n.m.r. spectra, that the cations in all of them have the *cis* configuration.

Experimental

Isolation of Solid Compounds

In all cases, the compounds were isolated directly from the mother liquors of the reactions, and the crystalline species were identified by X-ray powder photography before any "recrystallisations". This gives identification of the basic reaction products, and a check that isomerisation does not occur on "recrystallisation".

The analytical data are listed in Table I. All compounds were orange–yellow or brown–yellow in colour, with no particular shade distinguishing the different species.

Preparations in the Co/bipy/NO_2^- System

$[Co(bipy)_2(NO_2)_2]NO_3 \cdot n\,H_2O$

Three distinct methods of preparation were used: (a) the method of Lambert and Mason[3] gave one crystalline species (β-form) as the initial product, and then after ~1 hr at 0° C, a second crop, which was a different crystalline species (α-form); (b) the method of Palade *et al.*[5] from *cis*-$[Co(bipy)_2Cl_2]Cl$ gave only the α-form; (c) a mixture of $Na_3[Co(NO_2)_6]$ (2.02 g), bipyridyl (1.56 g) and urea (0.60 g) in water (20 ml) was treated with HNO_3 (21 ml, 1*M*), and the mixture was heated on the steam-bath. After the reaction had subsided, the mixture was heated for a further 5 min, and set aside to cool. The yellow crystals were filtered off and washed with water.

Different preparations by this method gave either the α- or the β-form.

If the reaction was carried out at lower temperatures, especially in an ice-bath, other water-insoluble species

TABLE I. The Compounds Prepared, the Analytical Data, and the X-ray Powder Diffraction Patterns (2Θ in mm).

Compound	Analyses (%)								X-ray Data[a]
	Found				Calculated				
	C	H	N	Cl	C	H	N	Cl	
[Co(bipy)$_2$(NO$_2$)$_2$]Cl·7H$_2$O	38.3	4.7	13.3	5.8	38.4	4.8	13.5	5.7	7.85s, 8.45w, 11.57s, br, 14.45ms, 15.12w, 16.70m, 17.80m, 21.50m, 24.75m, 25.60mw, 26.25m, 27.45m, 31.27ms
α-[Co(bipy)$_2$(NO$_2$)$_2$]NO$_3$·3H$_2$O	42.5	3.2	17.6		42.8	3.6	17.5		10.45w, 11.85vs, 14.75s, 15.80mw, 17.60w, 18.50ms, 20.40m, 21.00w, 21.60m, 23.55m, 26.80ms, 30.45s
β-[Co(bipy)$_2$(NO$_2$)$_2$]NO$_3$·3H$_2$O	43.1	3.2	17.7		42.8	3.6	17.5		7.90s, 11.15s, 11.85ms, 14.10ms, 14.95vw, 16.70ms, 17.50m, 21.40m, 23.75mw, 25.50m, br, 27.15m
α-[Co(bipy)$_2$(NO$_2$)$_2$]ClO$_4$	42.7	3.2	14.6	6.2	42.7	2.9	14.9	6.3	10.40s, 11.15s, 12.10m, 14.00m, 15.40vw, 16.90ms, 17.65vs, 18.80m, 24.00m, 24.30ms, 25.45s
β-[Co(bipy)$_2$(NO$_2$)$_2$]ClO$_4$	42.4	2.8	14.6	6.4	42.7	2.9	14.9	6.3	7.60m, 11.00ms, 12.75s, 13.95s, 15.10vw, 16.00m, 16.70ms, 18.25w, 19.05ms, 24.40m, 25.40s
[Co(bipy)$_2$(NO$_2$)$_2$][Co(bipy)(NO$_2$)$_4$]·8H$_2$O	36.3	3.1	16.5		35.8	4.0	16.7		7.00m, 13.00ms, 14.95s, 15.60m, 16.75w, 18.70mw, 20.80mw, 22.70mw, 25.00ms
[Co(phen)$_2$(NO$_2$)$_2$]Cl·3H$_2$O	47.3	4.0	13.8	5.0	48.0	3.7	14.0	5.9	9.20w, 9.90w, 12.50ms, br, 12.85s, 14.50ms, 16.30w, 21.45m, 24.00m, 25.50m, 28.60ms, 29.30m, 29.95ms
[Co(phen)$_2$(NO$_2$)$_2$]NO$_3$·2H$_2$O	47.5	3.2	15.8		47.3	3.3	16.1		9.00vw, 9.90w, 12.20ms, 12.75s, 13.40w, 14.50ms, 20.50m, 21.65m, 23.85mw, 25.70m, 29.30m, 29.95ms

$[Co(phen)_2(NO_2)_2][H(NO_3)_2] \cdot 2H_2O$		42.8	3.1	16.3		42.9	3.1	16.7		9.80w, 12.10s, 13.40m, 13.95w, 14.50m, 16.60mw, 21.60m, 22.70m, 26.45m, 29.90s, 38.85m, 43.75m
α-$[Co(phen)_2(NO_2)_2]ClO_4 \cdot H_2O$		46.3	3.2	13.5	5.9	45.8	2.9	13.4	5.6	10.85s, 11.50w, 13.45m, 16.00w, 17.10s, 17.80w, 18.80m, 19.95mw, 23.15m, 27.00mw, 30.15m
,,	product I[b]	46.1	3.0	13.4	5.6					c
,,	product II	46.0	3.4	13.0	5.6					c
,,	product III[d]	51.1	2.5	11.3	7.6					c
,,	product IV									c
,,	product V[e]	49.7	3.1	10.9	8.9					c

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[a] The first six lines are given together with up to six more of the stronger higher angle lines. [b] These were the products of other attempts at preparing $[Co(phen)_2(NO_2)_2]ClO_4$ – see text. [c] See Figure 2. [d] This product may contain some of $[Co(phen)_2(H_2O)(NO_2)](ClO_4)_2$. [e] This product contains some of the tris-chelated compound.

were obtained, which contain less than two moles of bipyridyl. The reaction (effervescence) takes *ca.* 2 hr for completion at 5° C, and the product is a mixture (X-ray data), one component of which is relatively soluble in water and the other not. The latter, obtained by continued washing of the reaction product (or by isolating the reaction product after only 10 min.), appears to be $[Co(bipy)_2(NO_2)_2][Co\ bipy(NO_2)_4]$ nH_2O. These products are unstable emitting oxides of nitrogen slowly at ambient temperature.

$[Co(bipy)_2(NO_2]Cl \cdot 7H_2O$

This compound was prepared by the method of Palade *et al.*[5]

$[Co(bipy)_2(NO_2)_2]ClO_4$

When aqueous solutions of α- or β-$[Co(bipy)_2(NO_2)_2]NO_3$ or of $[Co(bipy)_2(NO_2)_2]Cl$ were treated with $NaClO_4$, only one crystalline compound – α-$[Co(bipy)_2(NO_2)_2]ClO_4$ – was obtained. However, other preparative methods gave a second crystalline species (β-form):

(a) $[Co(H_2O)_6](ClO_4)_2$ (0.77 g) in water (10 ml) was treated with $NaNO_2$ (0.35 g), and then bipyridyl (0.64 g) in a mixture of methanol (5 ml) and glacial acetic acid (1 ml) was added slowly. The initial pink precipitate soon turned orange, and finally yellow–brown. After several hours the solid was filtered off, and washed with ethanol and ether. It was a mixture of the α and β-forms.

Recrystallisation from hot water, with subsequent addition of $NaClO_4$, gave the α-form in low yield. From the filtrates, however, when a large excess of $NaClO_4$ was added, bright yellow prisms of $[Co(bipy)_3](ClO_4)_3$ were obtained in high yield. For most efficient recrystallisation of these compounds, $NaNO_2$ should be added, and the heating limited.

(b) A second preparation as above, but using larger quantities (5 times) and ethanol instead of methanol, gave the β-form. Again recrystallisation from water gave the α-form.

Large amounts of $[Co(bipy)_3](ClO_4)_3$ were isolated from the reaction filtrates after the addition of $NaClO_4$.

The ^1H n.m.r. spectra show that the β-form here is invariably contaminated (~5–10%) with the tris-compound.

Preparations in the Co/phen/NO_2^- System

$[Co(phen)_2(NO_2)_2]NO_3 \cdot 2H_2O$

The method of Lambert and Mason[3] gave a mixture of this compound, and a second crystalline compound which we tentatively identify as an "acid nitrate" $[Co(phen)_2(NO_2)_2][H(NO_3)_2] \cdot 2H_2O$.

A preparation by Ablov's method[2] gave a reasonably pure sample of the hydrate as the initial product; but a preparation[3] from $[Co(phen)_2Cl_2]Cl$ in water gave a mixture of the nitrate and the chloride. Several recrystallisations of the product in the presence of some $NaNO_2$ and an excess of $NaNO_3$ were necessary for a pure preparation by the latter method.

Preparations were made also from $Na_3[Co(NO_2)_6]$, as for bipyridyl. Here, the reaction on the steam-bath resulted in the hydrate; and the reaction at 5° C in an ice-bath gave the second crystalline form which appears to be the dinitratohydrogen(I) species. From a reaction at room temperature, a mixture of both was obtained, as in the Lambert and Mason[3] method. The same products were obtained using $Na_3[Co(CO_3)_2(NO_2)_2]$[6] instead of the hexanitro compound.

$[Co(phen)_2(NO_2)_2]Cl \cdot 3H_2O$

A solution of *cis*-$[Co(phen)_2Cl_2]Cl$ in water was treated with $NaNO_2$, and the yellow precipitate was filtered off and washed with water. It was recrystallised by dissolving in hot water in the presence of $NaNO_2$, and adding LiCl to the hot solution.

$[Co(phen)_2(NO_2)_2]ClO_4$

The α-form was obtained by adding $NaClO_4$ to an aqueous solution of the nitrate, or the dinitratohydrogen(I) compound.

The other products, whose X-ray diffraction patterns are represented in Figure 2, were obtained as follows:

Products I and II. A solution of *cis*-$[Co(phen)_2Cl_2]Cl$ (0.6 g) in water (40 ml) was treated with $NaNO_2$ (0.2 g). After 1 hr, the yellow precipitate of crude $[Co(phen)_2(NO_2)_2]Cl$ was filtered off, washed, and redissolved in warm water. $NaClO_4$ was then added to precipitate the perchlorate. One crop was obtained by filtering off immediately (I) and a second after the filtrate had been set aside for 1 hr (II).

Products III and IV. These were obtained by the Ablov[3] procedure, substituting cobalt(II) perchlorate for cobalt(II) nitrate. The orange–yellow precipitate was recrystallised from hot water (III). A further small crop was obtained when the filtrate from the original reaction mixture was set aside for 2 days (IV).

Product V. This was prepared by the Lambert and Mason method[3], substituting cobalt(II) perchlorate and perchloric acid for cobalt(II) nitrate and nitric acid, respectively. The ^1H n.m.r. spectrum shows that it is contaminated with approx. 25% of the tris-phenanthrolinecobalt(III) perchlorate.

Physical Measurements

The following instruments were used: *X-ray diffraction,* Phillips 11.46 cm Debye–Scherrer camera with CoKα radiation; *i.r. spectra,* Perkin–Elmer PE 457; *electronic spectra,* Unicam SP700 with SP735 (diffuse reflectance) and Perkin–Elmer Ultracord 137 UV; and *^1H n.m.r. spectra,* Varian HA100.

Results and Discussion

As in the study of the chloro species,[7] we have first identified the various crystalline species obtainable by the X-ray diffraction patterns (Table I); and then have looked at the evidence for structure of the cation in each of the defined crystalline species.

Compounds were prepared by all published methods, and some new ones; and perchlorates have been prepared since this anion often precipitates cations that are not otherwise obtainable. Preparations from $[Co(NO_2)_6[^{3-}$ provide a convenient route to pure products.

The various reactions did give different crystalline species; but, as in the case of the chloro analogues,[7] these are simply different crystalline forms of the same *cis* compounds.

I.r. spectra were recorded in each case, and they were consistent with the formulations, but no other useful structural inferences can be drawn from them.[1]

$[Co(bipy)_2(NO_2)_2]X$ ($X = Cl$, NO_3 and ClO_4)

Both the nitrate and the perchlorate were obtained in two different crystalline forms. The β-forms of each appear from their X-ray diffraction patterns (Table I) to be essentially isomorphous, but there is no obvious relationship between the diffraction patterns of the α-forms. Several other crystalline species were detected in the products of the preparations from $[Co(NO_2)_6]^{3-}$, but these have been identified as containing monochelated species. In addition, trisbipyridylcobalt(III) perchlorate was a common contaminant of the perchlorates. It was readily detected by its X-ray diffraction pattern, or more sensitively in the ^1H n.m.r. spectra.

All compounds containing the dinitrobisbipyridylcobalt(III) cation give closely related ^1H n.m.r. spectra in $(CH_3)_2SO$ (Table II and Figure 1). These spectra can be analysed on a first-order basis (although there is also *meta* and *para* coupling which we have not attempted to analyse) as shown in Table II; and the minor differences between them are attributable to ion-pairing of the same cation with the different anions (see below). The assignments in Table II are the same as those[8] for *cis*-$[Ir(bipy)_2Cl_2]^+$. They are based on arguments similar to those used in this reference,[8] supported by spin-decoupling experiments, and a 220 MHz spectrum of $[Co(bipy)_2(NO_2)_2]NO_3$, which gives a better separation of the different resonances. The upfield (ring-current) shifts of the resonances of one of the pyridyl moieties[8] give unequivocal evidence for the *cis* configuration of the cations; and the spectra give no indication of the existence of significant amounts of the alternative *trans* species.

The differences observed in the spectra of the different salts of the $[Co(bipy)_2(NO_2)_2]^+$ cation in DMSO can be explained readily by the formation of specific ion-pairs; and indeed the spectra give evidence for the geometry of these ion-pairs. The resonances which change most between the different salts are the ones remote from the metal. This suggests (not surprisingly!) that in the ion-pair the anion is positioned against the bipyridyl ligands, at the position most remote from the nitro groups of the cation. Not surprisingly also, the spectrum of the chloride differs from those of the nitrate and perchlorate more than the latter two do from each other.

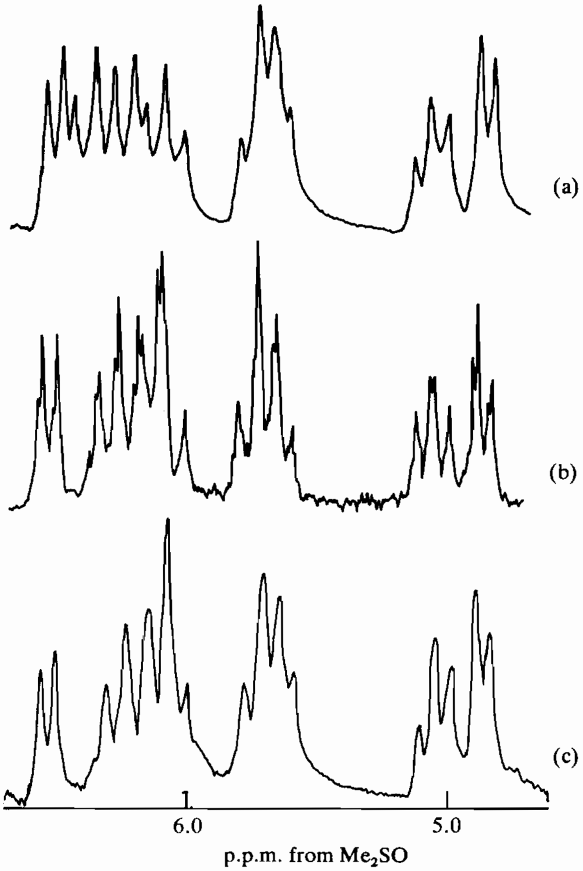
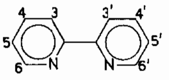
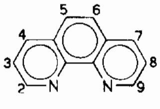


Figure 1. The ^1H n.m.r. spectra in $(CH_3)_2SO$ of $[Co(bipy)_2(NO_2)_2]X$: where $X = Cl$ for (a), NO_3 for (b), and ClO_4 for (c).

The electronic spectra of such $[CoN_6]$ chromophores cannot be expected to give evidence for configuration; although there is a basic requirement, if only *cis* isomers exist, that no differences should be observable between the visible spectra of the different compounds containing the $[Co(bipy)_2(NO_2)_2]^+$ cation. In keeping with this, we find no measureable differences between the visible spectra of the various bis-bipyridyl compounds. From the spectra also we find no evidence for nitrito species here. The *d–d* band is observed at 445 nm ($\lambda_{max} = 300$) in water, but it is only an unresolved shoulder in $(CH_3)_2SO$ solutions and in the diffuse reflectance spectra. In addition, ligand bands are observed in the ultra-violet at 350 (shoulder), 318 (shoulder) and 308 nm.

TABLE II. The ^1H N.m.r. Spectra (p.p.m. from Dimethylsulphoxide).

Compound	Resonances, Multiplicities and Assignments[a]								
	*6(d)*	*3(d)*	*3'(d)*	*4(t)*	*4'(t)*	*5(t)*	*5'(t)*	*6'(d)*[b]	
$[Co(bipy)_2(NO_2)_2]Cl \cdot 7H_2O$	6.53	6.42	6.27	6.11	5.75	5.69	5.08	4.87	$J_{3,4} \approx J_{4,5} \approx 8$ Hz
$[Co(bipy)_2(NO_2)_2]NO_3 \cdot 3H_2O$	6.53	6.30	(6.13)[c]	(6.10)[c]	5.73	5.65	5.05	4.86	$J_{3,5} \approx J_{4,6} \approx 1.5$ Hz
$[Co(bipy)_2(NO_2)_2]ClO_4$	6.54	6.28	(6.12)[c]	(6.08)[c]	5.71	5.65	5.05	4.86	$J_{5,6} \approx 6$ Hz
	Assignment		Observed Resonances[d]				Analyses		
$[Co(phen)_2(NO_2)_2]Cl \cdot 3H_2O$	5, 6		5.75	5.846	5.912	5.998	$\nu_5 = 5.942$		$J_{5,6} = 8.9$ Hz[e]
							$\nu_6 = 5.816$		
	2, 3, 4	(A)	7.038	7.028	6.983	6.975	$\nu_2 = 7.006$		$J_{2,3} = 5.5$ Hz
		(M)	6.838	6.828	6.757	6.748	$\nu_3 = 6.047$		$J_{2,4} = 1.0$ Hz
		(X)	6.116	6.058	6.033	5.978	$\nu_4 = 6.793$		$J_{3,4} = 8.1$ Hz
	7, 8, 9	(AB)	5.277	5.224	5.202	5.149	$\nu_7 = 6.331$		$J_{8,9} = 5.3$ Hz
			5.132	5.094	5.075	[f]			$J_{7,8} + J_{7,9} = 9.3$ Hz
		(X)	6.378	6.362	6.302	6.285			
$[Co(phen)_2(NO_2)_2]NO_3 \cdot 2H_2O$	5, 6		5.967	5.878	5.817	5.728	$\nu_5 = 5.908$		$J_{5,6} = 8.9$ Hz
							$\nu_6 = 5.787$		
	2, 3, 4	(A)	7.019	7.009	6.963	6.953	$\nu_2 = 6.990$		$J_{2,3} = 5.6$ Hz
		(M)	6.778	6.768	6.697	6.687	$\nu_3 = 6.008$		$J_{2,4} = 1.0$ Hz
		(X)	6.076	6.021	5.995	5.938	$\nu_4 = 6.737$		$J_{3,4} = 8.15$ Hz
	7, 8, 9	(AB)	5.248	5.195	5.174	5.120	$\nu_7 = 6.280$		$J_{8,9} = 5.25$ Hz
			5.110	5.068	5.052	[f]			$J_{7,8} + J_{7,9} = 9.3$ Hz
		(X)	6.326	6.309	6.249	6.233			
$[Co(phen)_2(NO_2)_2]ClO_4 \cdot H_2O$	5, 6		5.980	5.894	5.832	5.740	$\nu_5 = 5.924$		$J_{5,6} = 8.9$ Hz[e]
							$\nu_6 = 5.802$		
	2, 3, 4	(A)	7.048	7.038	6.992	6.987	$\nu_2 = 7.015$		$J_{2,3} = 5.55$ Hz
		(M)	6.792	6.782	6.710	6.700	$\nu_3 = 6.030$		$J_{2,4} = 1.0$ Hz
		(X)	6.098	6.042	6.017	5.962	$\nu_4 = 6.746$		$J_{3,4} = 8.1$ Hz
	7, 8, 9	(AB)	5.268	5.216	5.195	5.142	$\nu_7 = 6.291$		$J_{8,9} = 5.2$ Hz
			5.128	5.088	5.07	[f]			$J_{7,8} + J_{7,9} = 9.3$ Hz
		(X)	6.337	6.320	6.262	6.244			

[a] Assignments refer to the numbers of the diagrams. The protons subject to ring-current de-shielding are the primed set for bipyridyl, and the higher numbers for phenanthroline. [b] d = doublet, t = triplet. Fine structure resulting from *meta* and *para* coupling also was observed, but not analysed. [c] Because of overlap these signals are not precisely defined. [d] Relative intensities were all very close to those of Figure 3. [e] These are averages of the two observed separations of 8.6 and 9.2 Hz. [f] There is a lot of overlap of signals here so that one component of the AB set is not resolved and several are poorly defined.

It is the latter band which Gomwalk and McAuley[4] followed in their kinetic study of the acid hydrolysis. Reinterpreting their data in the light of the present work, we can say that the first step they observed is:

$$cis\text{-}[Co(bipy)_2(NO_2)_2]^+ + H_2O \rightarrow cis\text{-}[Co(bipy)_2(H_2O)(NO_2)]^{2+} + NO_2^-$$

and the second step is a disproportionation to the tris-chelated species. Compelling evidence for the latter is given by our isolation of large amounts of $[Co(bipy)_3](ClO_4)_3$ from the filtrates of the recrystallisation of the bis species. The spectral changes reported[4] are also best interpreted in these terms. It is not correct to compare the UV spectra of cobalt–ammines with those of these bipyridyl compounds. $[Co(bipy)_3]^{3+}$ has (asymmetric) bands at 300 and 309 nm (ligand $\pi \rightarrow \pi^*$ transitions), with the former the more intense, and it is undoubtedly causing the reported[4] spectral shift (from 310→303 nm).

$[Co(phen)_2(NO_2)_2]X$ (X = Cl, NO_3 and ClO_4)

In addition to *cis*-$[Co(phen)_2(NO_2)_2]NO_3 \cdot 2H_2O$, first reported by Ablov,[2] we have obtained another crystalline species. The latter appears to be an "acid nitrate" *cis*-$[Co(phen)_2(NO_2)_2][H(NO_3)_2] \cdot 2H_2O$, and gives the same ^1H n.m.r. spectrum in $(CH_3)_2SO$ as the simple nitrate. The proton is assigned to the dinitratohydrogen(I) species by analogy with well-characterised species of this type.[9]

A variety of perchlorates were obtained, but only one of them (the α-form) in what we are certain is a pure form. The X-ray powder diffraction patterns of five other representative products are represented in Figure 2. Of these, products I and II appear to represent almost pure samples of a second crystalline form; and product III may contain some of *cis*-[Co(phen)$_2$(H$_2$O)(NO$_2$)](ClO$_4$)$_2$. The important point, however, is that in (CH$_3$)$_2$SO solution all of them and the various other salts gave essentially the same ^{1}H n.m.r. spectra (Figure 3) which prove the *cis* configuration (see ref. 10). Except for product V, which contained some [Co(phen)$_3$]$^{3+}$, no other phenanthroline species was detectable in these spectra. The tris-species has a characteristic spectrum[11] which cannot be confused with that expected for the hypothetical *trans*-isomer of the bis-chelated species.

As in the case of the bipyridyl compounds, specific ion-pairing causes small but significant variations in the ^{1}H n.m.r. spectra of the different salts. The 100 MHz spectra consist (Table II) of an AB system for protons 5and 6 (atom labelling is the same as in ref. 10); an AMX system for protons 2, 3 and 4; and an ABX system for the other three protons 7, 8 and 9. Because of overlap of some of the signals we have not attempted a complete analysis of the ABX systems; but all assignments were confirmed by spin decoupling experiments, and by a 220 MHz spectrum of the nitrate. The AB systems of protons 5 and 6 are not symmetrical – indicating perhaps some weak spin–spin interactions with other protons of the molecule.

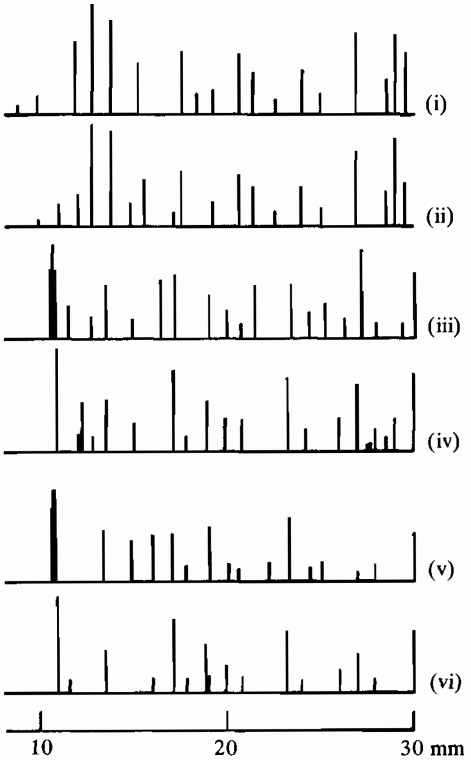


Figure 2. The X-ray powder diffraction patterns of the various products from the preparations of [Co(phen)$_2$(NO$_2$)$_2$]ClO$_4$. (i) = Product I; (ii) = Product II; (iii) = Product III); (iv = Product IV; (v) = Product V; (vi) = α-[Co(phen)$_2$(NO$_2$)$_2$]ClO$_4$.

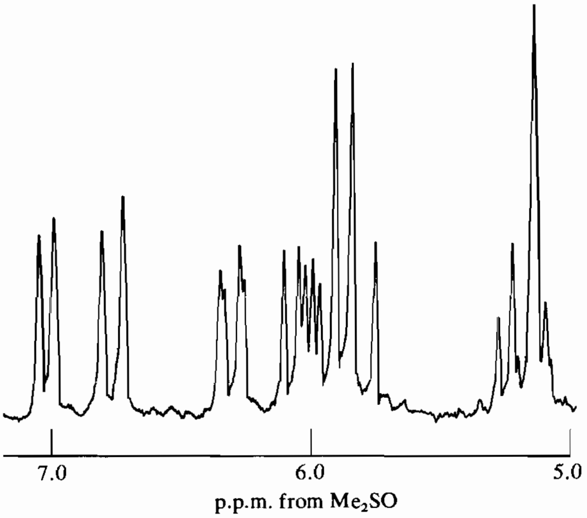


Figure 3. The ^{1}H n.m.r. spectrum in (CH$_3$)$_2$SO of [Co(phen)$_2$(NO$_2$)$_2$]NO$_3$·2H$_2$O.

The only *d–d* band observed in the electronic spectra is a barely resolved band at 450 nm in water. As in the case of the bipyridyl compounds, we did not observe any species with a *d–d* band at lower energy which might be indicative of a nitrito species.

Thus, more or less as expected, we have been able to obtain only *cis* isomers of the dinitro species. In addition, although we have looked for them, we have found no evidence for nitrito isomers of these cations.

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