Ru(facac)H(CO)$(PPh_3)_2$(IIc), 64625-62-3; Ru(facfac)H(CO)$(PPh_3)_2$, 64567-30-2; $Ru(acac)_2(PPh_3)_2$, 26455-78-7; $Ru(facac)_2(PPh_3)_2$, 64625-08-7; $R(facfac)_2(PPh_3)_2$, 64567-38-0; Os(acac)H(CO)$(PPh_3)_2$, 61950-99-0; Os(facac)H(CO)$(PPh_3)_2$(IIb), 64625-07-6; Os(facac)H(CO)$(PPh_3)_2$(IIc), 64567-37-9; Os(facfac)H(CO)$(PPh_3)_2$, 64567-36-8; $Os(acac)_2(PPh_3)_2$, 64567-35-7; $Os(facac)_2(PPh_3)_2$, 64567-34-6; $Os(facfac)_2(PPh_3)_2$, 64567-33-5; Ir(acac)ClH$(PPh_3)_2$, 64567-32-4; Ir(acac)$H_2(PPh_3)_2$, 64625-61-2; Ir(facac)$H_2(PPh_3)_2$, 64625-06-5; Ir(facac)$H_2(PPh_3)_2$, 64625-05-4; RuClH(CO)$(PPh_3)_3$, 16971-33-8; $RuH_2(CO)(PPh_3)_3$, 25360-32-1; $Ru(CO)_3(PPh_3)_2$, 14741-36-7; $RuH_2(PPh_3)_4$, 19529-00-1; OsClH(CO)$(PPh_3)_3$, 16971-31-6; $OsH_2(CO)(PPh_3)_3$, 12104-84-6; $OsH_4(PPh_3)_3$, 24228-59-9; *mer*-$IrH_3(PPh_3)_3$, 18660-46-3; $IrCl_2H(PPh_3)_3$, 16971-01-0.

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Synthesis and Circular Dichroism Studies of Isoelectronic Complexes: Tetracyanoferrate(II) and Tetracyanocobaltate(III) with (*R*)-1,2-Diaminopropane and (*R*,*R*)-*trans*-1,2-Diaminocyclohexane Chelates

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The preparation of diamagnetic isostructural and isoelectronic tetracyanoferrate(II) and tetracyanocobaltate(III) with optically active (*R*)-1,2-diaminopropane and (*R*,*R*)-*trans*-1,2-diaminocyclohexane is reported. Absorption, circular dichroism (CD), and ^{1}H NMR spectra are reported. The three visible components of the CD in the spectra of a Fe(II) complex have similar origins to the corresponding components of the Co(III) analogue.

Circular dichroism (CD) spectra have been measured for a variety of Co(III) complexes,[1] but there have been few reports on CD spectra of other d^6 metal complexes. In particular, no reports are available on diamagnetic Fe(II) complexes except those with certain conjugated ligands such as *o*-phenanthroline (phen) and 2,2′-bipyridyl (bpy). CD spectra of $Fe(phen)_3^{2+}$ and $Fe(bpy)_3^{2+}$ have been studied in terms of the exciton approach to deduce the absolute configuration.[2] These complexes have intense charge-transfer (CT) absorptions in the visible region which obscure d–d transitions.[2] The structural investigations of transition-metal complexes will be aided and expanded by investigation of CD spectra of isoelectronic and isostructural metal complexes. Since Fe(II) and Fe(III) ions are biologically important, a knowledge of the application of CD methods to model systems may someday allow CD techniques to be applied to the structural understanding of Fe complexes in biological systems. The first step in the elucidation of the CD spectra of Fe(II) complexes is a comparison of diamagnetic Fe(II) complexes with those of Co(III) complexes. Fe(II) complexes having an optically active diamine as the sole source of dissymmetry are especially suited to study because their CD spectra may be compared with those of Co(III) complexes for which a vast quantity of data has been accumulated. Tetracyanodiamineferrate(II) complexes have been shown to be diamagnetic[3] and isostructural with the corresponding cobalt(III) complexes.[4] Optically active derivatives of these complexes can be prepared with resolved diamines, (*R*)-1,2-diaminopropane (*R*-pn) and (*R*,*R*)-*trans*-1,2-diaminocyclohexane (*R*-chxn). The preparation and characterization of this type of new complexes are reported herein, and their CD spectra are reported in detail.

Experimental Section

Materials. Commercially available 1,2-diaminopropane, pn, was resolved into *R*-pn by the method of Dwyer;[5] $[\alpha]^{23}{}_D$ −33.6° (benzene). 1,2-Diaminocyclohexane (Tokyo Kasei) was resolved into the (*R*,*R*)-trans isomer, *R*-chxn, by the method of Jaeger and Bijkerk;[6] $[\alpha]^{23}{}_D$ −43.0° (free diamine, 3% methanol solution), lit.[7] $[\alpha]^{24}{}_D$ −44.1°. Ferrous perchlorate hexahydrate (Alfa) was used without further purification. Potassium bromopentacyanocobaltate(III) was prepared by the method of Adamson[8] from cobaltous acetate and 5 equiv of KCN followed by oxidation with bromine. The purity of this compound was found to be ca. 70% from optical absorbance at 395 nm, but it was used to prepare subsequent complexes without further purification because of lack of a method for recrystallization.[9]

Preparation of Tetracyano Complexes. Sodium Tetracyano(*R*-pn)ferrate(II)·0.5H$_2$O·0.5NaClO$_4$. A methanol solution (40 mL) of *R*-pn (14.5 g, 0.2 mol) was added to a methanol solution (200 mL) of ferrous perchlorate hexahydrate (35.2 g, 0.098 mol) with vigorous stirring under nitrogen at 0 °C, followed by the addition of aqueous sodium cyanide (19.1 g, 0.195 mol) in 80 mL of water. The resultant yellow-brown solution was concentrated to near dryness under reduced pressure below 40 °C. To the oily residue, ethanol (40 mL) was added, and a yellow precipitate was collected on a filter and washed with ethanol and ether; yield 29.4 g (87%). The crude product was recrystallized by dissolving it in 35 mL of water, followed by the addition of a 1:2 methanol ethanol mixture (180 mL) at 30 °C and letting the mixture stand overnight in a refrigerator. Anal. Calcd for $Na_2[Fe(C_3H_{10}N_2)(CN)_4]\cdot 0.5H_2O\cdot 0.5NaClO_4$: C, 24.90; H, 3.16; N, 24.25. Found: C, 24.00; H, 3.16; N, 23.99.[10]

Sodium Tetracyano(*R*-chxn)ferrate(II)·0.5H$_2$O·0.5NaClO$_4$. The same procedure was used as for the above preparation; yield 27.0 g

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(69%). The crude product was recrystallized from a 1:8 H_2O–ethanol mixture. Anal. Calcd for $Na_2[Fe(C_6H_{14}N_2)(CN)_4]\cdot 0.5H_2O\cdot 0.5NaClO_4$: C, 31.25; H, 4.29; N, 21.39. Found: C, 30.77; H, 3.87; N, 21.53.[10]

Potassium Tetracyano(*R*-pn)cobaltate(III)·1.5H_2O. This complex was prepared by a modification of the procedure of Yano et al.[11] A more precise procedure is described below. To an aqueous solution of $K_3[Co(CN)_5Br]$ (7.72 g, 0.02 mol) in 20 mL of water, *R*-pn (3 mL) was added, and the mixture was stirred at 80 °C for 1 h while the color of the solution changed from dark red to yellow. The resultant solution was concentrated to near dryness, and the complex was precipitated with ethanol. This precipitate was collected on a filter and washed with ethanol thoroughly. The pale yellow precipitate was extracted with methanol (80 mL), and the mixture was filtered to remove undissolved materials. To the filtrate, ethanol (140 mL) was added, and the mixture was allowed to stand in a refrigerator overnight. A white crystalline material, presumably the aquocyano complex, formed and was filtered off. The filtrate was concentrated to near dryness again. The resultant yellow residue was dissolved in a 1:4 H_2O–methanol mixture (22 mL), the solution was warmed to 50 °C, and ethanol (95%) was added until the solution became turbid. The mixture was allowed to stand overnight, and pale yellow crystals were collected on a filter and washed with ethanol and ether; yield 1.2 g. Anal. Calcd for $K[Co(C_3H_{10}N_2)(CN)_4]\cdot 1.5H_2O$: C, 28.09; H, 4.24; N, 28.00. Found: C, 27.73; H, 4.32; N, 27.71.

Potassium Tetracyano(*R*-chxn)cobaltate(III)·1.5H_2O. To an aqueous solution of $K_3[Co(CN)_5Br]$ (7.72 g) in 20 mL of water, *R*-chxn (3.5 g in 10 mL of water) was added, and the mixture was stirred for 30 min at 55 °C. The mixture was concentrated to near dryness under reduced pressure. The complex was precipitated by adding ethanol (50 mL) to the residue. A yellow precipitate formed which was collected on a filter. This was extracted twice with 150 mL of methanol, and the solution was concentrated again. The residue was dissolved in absolute methanol (40 mL), and the undissolved materials were filtered off. To the filtrate, 80 mL of 95% ethanol was added with warming, and the mixture was placed in a refrigerator and allowed to stand overnight. Pale yellow needles were collected on a filter and washed with ethanol; yield 0.9 g. This was recrystallized from a water (6 mL)–ethanol (50 mL) mixture; yield 0.6 g. Anal. Calcd for $K[Co(C_6H_{14}N_2)(CN)_4]\cdot 1.5H_2O$: C, 35.37; H, 5.01; N, 24.16. Found: C, 34.99; H, 4.99; N, 24.48.

Physical Measurements. Electronic spectra of aqueous solutions were recorded with a Shimadzu UV-200 spectrophotometer. CD spectra were measured with a Jasco J-40 recording polarimeter using aqueous solutions of the complexes. Proton magnetic resonance (^1H NMR) spectra were measured with a Jeol JNM-MH-100 spectrometer using D_2O or ca. 1 N NaOH–D_2O solutions and sodium 2,2-dimethyl-2-silapentanesulfonate (DSS) as an internal standard. Infrared spectra were measured with a Jasco IRA-2 recording spectrometer using KBr disks.

Results and Discussion

Optically active diamagnetic Fe(II) complexes were prepared by a manner similar to some other tetracyanodiamineferrate(II) complexes[3] but optically active diamine ligands were used. The new complexes are yellow crystalline solids and air stable. They are diamagnetic as evident from their ^1H NMR spectra, shown in Figure 1. Isoelectronic and isostructural complexes of Co(III) were prepared by a method similar to that of Yano et al.[11] Their ^1H NMR spectra are represented in Figure 1 for comparison.

The schematic structures of the complexes and the numbering of protons are shown in Figure 2. The ^1H NMR spectrum of $[Co(R\text{-pn})(CN)_4]^-$ has been fully analyzed, and the chelate ring or coordinating *R*-pn has been reported to be fixed with the methyl group located equatorial to the chelate ring.[11] The conformation of the chelate ring is λ from the absolute configuration of *R*-pn. The corresponding $[Fe(R\text{-pn})(CN)_4]^{2-}$ species exhibits signals at 1.22 (methyl, doublet), 2.11 (H_{2a}, a pair of doublets), 2.62 (H_{2a}), and 2.72 ppm (H_{1a}) from DSS. The conformation of the Fe(II) complex has been determined to be λ from the similarity of the ^1H NMR spectrum, particularly the pair of doublets of H_{2a} indicates that the conformation of the chelate ring is fixed.

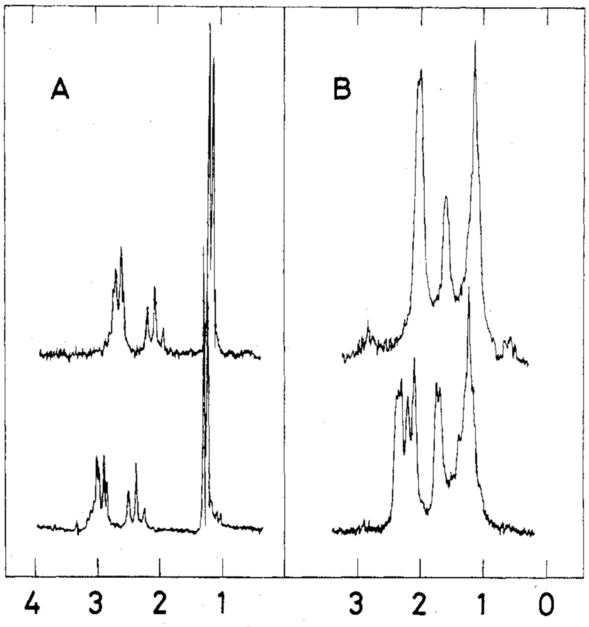

Figure 1. ^1H NMR spectra of $[Fe(R\text{-pn})(CN)_4]^{2-}$ (A, upper), $[Co(R\text{-pn})(CN)_4]^-$ (A, bottom), and $[Fe(R\text{-chxn})(CN)_4]^{2-}$ (B, upper) in D_2O and $[Co(R\text{-chxn})(CN)_4]^-$ (B, bottom) in 0.1 N NaOH–D_2O.

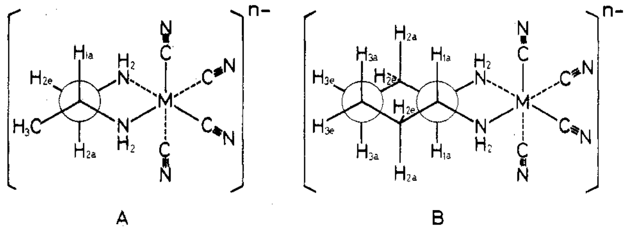

Figure 2. Schematic structures of $[M(R\text{-pn})(CN)_4]^{n-}$ (A) and $[M(R\text{-chxn})(CN)_4]^{n-}$ (B) and the numbering of protons.

The ^1H NMR spectra of $[Fe(R\text{-chxn})(CN)_4]^{2-}$ and $[Co(R\text{-chxn})(CN)_4]^-$ are also very similar to each other, as shown in Figure 1. The spectra are composed of multiplets, as expected for a fixed cyclohexane ring conformation. The resonances of each proton experience an anisotropic magnetic environment produced from the coordinated $C{\equiv}N^-$ groups. The axial protons in the chelate ring appear at higher magnetic fields than the equatorial ones; as expected this effect diminishes with increasing distance from $C{\equiv}N^-$ groups. Four types of signals appeared at 1.21, 1.71, 2.17, and 2.35 ppm in the ratio of 2:1:1:1, respectively, for the Co(III) complex. H–D exchange of the coordinated amines of $[Co(R\text{-pn})(CN)_4]^-$ and $[Co(R\text{-chxn})(CN)_4]^-$ is slow, and N–H protons are observed at 3.93, 4.28, and 4.50 ppm and at 3.81 and 4.89 ppm, respectively, in D_2O. The N–H protons of $[Co(R\text{-chxn})(CN)_4]^-$ did not exchange with those of D_2O within 2 weeks after dissolving. Exchange was observed with ca. 0.1 N NaOH–D_2O solution after 2 h. This retardation is partly because of the negative charge of the complex, but the extremely slow exchange of $[Co(R\text{-chxn})(CN)_4]^-$ cannot be totally accounted for by the charge of the complex. The retardation of H–D exchange of amine coordinating to Co(III) by CN^- groups trans to amine has been reported by Yoneda et al.[12]

The axial protons of the methine carbon (H_{1a}) were assigned to the 2.35-ppm resonance on the basis of the sharpening of the signals upon deuteration of the amine. The methylene protons are subject to the anisotropy of the cyclohexane ring and of the $C{\equiv}N^-$ groups and are assigned to signals at 2.17

Table I. Maxima[a] of Electronic and CD Spectra of the $Co(CN)_n(N)_{6-n}^{(3-n)+}$ and $Fe(CN)_n(N)_{6-n}^{(2-n)+}$ Complexes

Complex	$^1A_{1g} \rightarrow {}^1T_{1g}$		$^1A_{1g} \rightarrow {}^1T_{2g}$		Charge transfer	
	$\tilde{\nu}_{max}$ (Log ϵ)	$\tilde{\nu}^{CD}_{max}$ ($\Delta\epsilon$)	$\tilde{\nu}_{max}$ (Log ϵ)	$\tilde{\nu}^{CD}_{max}$ ($\Delta\epsilon$)	$\tilde{\nu}_{max}$ (Log ϵ)	$\tilde{\nu}^{CD}_{max}$ ($\Delta\epsilon$)
$K_3[Co(CN)_6]$[b]	32.1 (2.39)		38.9 (2.26)		49.5 (4.28)	
$[Co(CN)_5(NH_3)]^{2-}$ [c]	29.0 (2.61)		37.3 (1.57)			
$K[Co(CN)_4(R\text{-pn})]\cdot 1.5H_2O$[d]	28.4 (2.32)	25.2 (−0.15) 28.8 (+0.67)	35.0 (2.07)	34.0 (−0.08) 37.0 (+0.04)	47.8 (4.38)	46.2 (+5.4)
$K[Co(CN)_4(R\text{-chxn})]\cdot 1.5H_2O$[d]	28.4 (2.30)	24.8 (−0.09) 28.6 (+1.01)	35.0 (2.05)	34.0 (−0.12) 37.5 (+0.05)	47.6 (4.36)	46.5 (+8.4)
trans-$[Co(CN)_2(R\text{-pn})_2]Cl$[e]	22 (*i*) 24.5 (1.80)	21.0 (−0.25) 24.7 (+1.07)	32.1 (1.80)	31.0 (−0.14)		
trans-$[Co(CN)_2(R\text{-chxn})_2]ClO_4$[e]	22 (*i*) 24.4 (1.83)	20.9 (−0.28) 24.5 (+2.28)	32.0 (1.84)	30.6 (−0.36)		
$[Co(en)_3](ClO_4)_3$[f]	21.3 (1.94)		29.5 (1.90)		47.3 (4.32)	
$K_4[Fe(CN)_6]\cdot 3H_2O$[b]	31.0 (2.48)		37.0 (3.0,*i*)		45.9 (4.39) 50.0 (4.37)	
$Na_3[Fe(CN)_5(NH_3)]\cdot 4.5H_2O$[g]	25.4 (2.61)		35.0[h] (2.8)[h]			
$Na_2[Fe(CN)_4(R\text{-pn})]\cdot 0.5H_2O\cdot 0.5NaClO_4$[d]	25.5 (2.61)	22.4 (−0.23) 26.0 (+0.36)	31.2 (2.63)	30.2 (−0.16)	43.6 (4.03)	37.0 (+1.0) 41.7 (+2.3)
$Na_2[Fe(CN)_4(R\text{-chxn})]\cdot 0.5H_2O\cdot 0.5NaClO_4$[d]	25.5 (2.61)	22.2 (−0.18) 26.0 (+0.51)	32.0 (2.66)	30.3 (−0.16)	44.8 (3.99)	37.0 (+0.6) 42.0 (+2.8)

[a] In 10^3 cm^{-1}. [b] Reference 15. [c] Prepared in situ; J. H. Bayston, R. N. Beale, N. K. King, and M. E. Winfield, *Aust. J. Chem.*, 16, 954 (1963). [d] Present study. [e] Reference 17. [f] Reference 4. [g] K. Shinra and I. Masuda, *Nippon Kagaku Zasshi,* 75, 1211 (1954). [h] For $Na_3[Fe(CN)_5(NH_2CH_3)]$. [i] Shoulder.

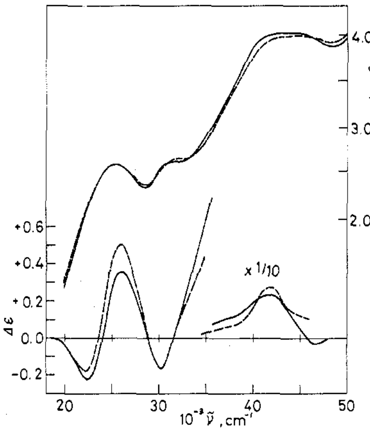

Figure 3. Electronic and CD spectra of $[Fe(R\text{-pn})(CN)_4]^{2-}$ (—) and $[Fe(R\text{-chxn})(CN)_4]^{2-}$ (--).

and 1.69 ppm for the equatorial (H_{2e} and H_{3e}) protons, respectively. The coupling constant (11 Hz) of the doublet at 2.17 ppm is consistent with the vicinal coupling constant. The remaining protons at 1.19 ppm were not well resolved. These are assigned to the axial methylene hydrogens (H_{2a} and H_{3a}).

The ^1H NMR spectrum of $[Fe(R\text{-chxn})(CN)_4]^{2-}$ showed three broad signals at ca. 2.1, 1.61, and 1.14 ppm with ratios of 2:1:2, respectively. By comparing these signals with those of the Co(III) complex, the former have been assigned as a composite of axial methine(H_{1a}) and equatorial methylene (H_{2e}) protons and equatorial methylene(H_{3e}) and axial methylene(H_{2a} and H_{3a}) protons, respectively. The chemical shifts of each proton from the Fe(II) complexes appear at slightly higher magnetic fields than those from the Co(III) complexes.

The infrared spectra of the Co(III) and Fe(II) complexes showed marked difference in the $C{\equiv}N^-$ stretching region with $C{\equiv}N$ stretching appearing at 2040 and 2125 cm^{-1} for the Fe(II) and Co(III) complexes, respectively. The decrease in wavenumber for the Fe(II) complexes is caused by a weakening of the $C{\equiv}N$ bond upon coordination, resulting from extensive back-donation from Fe(II).[13]

The CD and electronic spectra of the Fe(II) and Co(III) complexes are shown in Figures 3 and 4, respectively. Numerical data, along with several $[M(N)_n(CN)_{6-n}]^{m+}$ complexes, where M represents Fe(II) and Co(III), are listed in Table I.

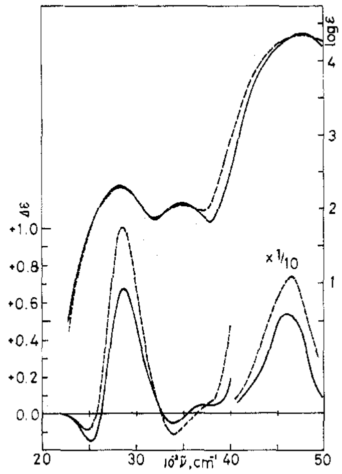

Figure 4. Electronic and CD spectra of $[Co(R\text{-pn})(CN)_4]^-$ (—) and $[Co(R\text{-chxn})(CN)_4]^-$ (--)

The electronic spectra of $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$ have been extensively studied along with several hexacyanometalates.[14,15] Both complexes have weak intensity ligand field absorption bands below 40 000 cm^{-1} and intense metal–ligand charge-transfer (MLCT) bands above 40 000 cm^{-1}. From these, the ligand field parameter, $10Dq$, is calculated to be 33 800 and 34 800 cm^{-1} for $[Fe(CN)_6]^{4-}$ and $[Co(CN)_6]^{3-}$, respectively.[14] The electronic spectra of $[Fe(R\text{-pn})(CN)_4]^{2-}$ and $[Fe(R\text{-chxn})(CN)_4]^{2-}$ have maxima at 25 500 (ϵ_{max} 407) and ca. 31 500 cm^{-1} (ϵ_{max} 440); these absorption bands are ascribed to LF absorptions. The nature of the metal–ligand bonding of Fe(II) and Co(III) can be deduced by comparing the shifts of these bands for the two metals. The $C{\equiv}N^-$ ligand has vacant π^* orbitals and is subject to back-donation from metal to ligand, while the nitrogen atoms of the amine group are pure σ-donor ligands. The shift is estimated from the perturbation theory of Yamatera for low-spin d^6 electron configuration.[16] Substitution of $C{\equiv}N^-$ by an amine ligand causes shifts which are composed of both σ and π effects. If the shift from $[M(CN)_6]^{n-}$ to $[MN_6]^{n+}$ is defined as δ, the first absorption band splits and appears at lower energy by a factor of $^1/_2\delta$ and $^1/_4\delta$ for *cis*-$[M(N)_2(CN)_4]^{n-}$ than the corresponding first absorption band of $[M(CN)_6]^{n-}$. These shifts are estimated approximately from the two maxima of the CD components, namely, 3600 cm^{-1} from the difference between the positive CD maximum for $[\mathrm{Co}(R\text{-diamine})(\mathrm{CN})_4]^-$ and the absorption maximum of the $[\mathrm{Co(CN)_6}]^{3-}$ and 3700 cm^{-1} from the difference between two CD maxima of the first absorption band of $[\mathrm{Co}(R\text{-diamine})(\mathrm{CN})_4]^-$. Two CD maxima of opposite signs also appear in the first absorption band for *trans*-$[\mathrm{Co}(R\text{-pn})_2(\mathrm{CN})_2]^+$ and *trans*-$[\mathrm{Co}(R\text{-chxn})_2(\mathrm{CN})_2]^+$.[17] The major positive CD component is shifted slightly more to a lower wavenumber than expected, but the deviations of the band positions are consistent with Yamatera's theory,[16] giving, 11 000 cm^{-1} as δ for Co(III) complexes. The same procedure leads to values of 5000 and 3600 cm^{-1} for Fe(II) complexes. If we take the mean of these values, 4300 cm^{-1}, for $^1/_4\delta$, the band shift caused by substitution of $\mathrm{C{\equiv}N^-}$ by an amine is larger for Fe(II) complexes. This is in agreement with the results of the infrared spectra, namely, the contribution of back-donation is larger for Fe(II) complexes than for Co(III) complexes. The same conclusion is derived from the LF formalism as discussed for several substituted pentacyanocobaltate(III) complexes.[9]

The shift of the second absorption band, originating from the $^1\mathrm{A}_{1g} \rightarrow {}^1\mathrm{T}_{2g}$ transition, is expected to be affected differently by σ and π effects from the perturbation theory.[16] The predicted shifts for this band are $^2/_3\delta_\sigma$ and $^1/_6\delta_\sigma + {}^1/_2\delta_\pi$ for *trans*-$\mathrm{MX_4Y_2}$ (D_{4h}) and $^5/_{12}\delta_\sigma + {}^1/_4\delta_\pi$ and $^1/_6\delta_\sigma + {}^1/_2\delta_\pi$ for *cis*-$\mathrm{MX_4Y_2}$ (C_{2v}). From the two CD components observed in the region of the second absorption band for $[\mathrm{Co}(R\text{-diamine})(\mathrm{CN})_4]^-$, values of ca. 11 000 cm^{-1} for δ_σ and -1000 cm^{-1} for δ_π with the ligand $\mathrm{C{\equiv}N^-}$ for the Co(III) complexes are derived. This indicates that the upper order of $\mathrm{C{\equiv}N^-}$ in the spectrochemical series is ascribed mainly to the σ effect as discussed above. The same situation is expected for the Fe(II) complexes, but a strong positive CD component obscures the second component of the CD absorption.

Strong bands appeared at ca. 43 000 and 47 800 cm^{-1} for the Fe(II) and Co(III) complexes, respectively, and were assigned to be MLCT transitions. The low-energy band for the Fe(II) complexes is in agreement with the expectation that the separation between the $\mathrm{T_{2g}}$ orbitals and the ligand antibonding orbitals is less for the Fe(II) complex than for the Co(III) complex. This has been shown by extended Hückel MO calculations for $[\mathrm{Co(CN)_6}]^{3-}$ and $[\mathrm{Fe(CN)_6}]^{4-}$.[15]

A striking similarity is observed for the CD spectra of $[\mathrm{Fe}(R\text{-diamine})(\mathrm{CN})_4]^{2-}$ and the corresponding Co(III) complexes as shown in Figures 3 and 4. The first absorption band splits into two CD components of opposite sign, a negative small component at lower wavenumber and a large positive component at higher wavenumber. The CD spectra of *trans*-$[\mathrm{Co}(R\text{-pn})_2(\mathrm{CN})_2]^+$ and *trans*-$[\mathrm{Co}(R\text{-chxn})_2(\mathrm{CN})_2]^+$ also have two CD components associated with the first absorption band.[17] The lower but still approximate symmetry of *trans*-$[\mathrm{Co}(R\text{-diamine})_2(\mathrm{CN})_2]^+$, D_{4h}, decomposes the first absorption band into $^1\mathrm{A}_{1g} \rightarrow {}^1\mathrm{A}_{2g}$ and $^1\mathrm{A}_{1g} \rightarrow {}^1\mathrm{E}_{1g}$ components. It has been well established from CD measurements on the first absorption band of *trans*-$[\mathrm{Co}(R\text{-pn})_2\mathrm{X}_2]^{n+}$ and *trans*-$[\mathrm{Co}(R\text{-chxn})_2\mathrm{X}_2]^{n+}$ that the sign of the $\rightarrow {}^1\mathrm{A}_{2g}$ component is negative and that of the $\rightarrow {}^1\mathrm{E}_{1g}$ component is positive.[18,19] The two CD components of *trans*-$[\mathrm{Co}(R\text{-diamine})_2(\mathrm{CN})_2]^+$ have been assigned to $\rightarrow {}^1\mathrm{A}_{2g}$ and $\rightarrow {}^1\mathrm{E}_{1g}$ transitions in order of increasing energy on the basis of the higher order of $\mathrm{C{\equiv}N^-}$ than amine in the spectrochemical series. The sign of each component is in agreement with established empirical rules.[17] The monodiamine complex $[\mathrm{Co}(R\text{-diamine})(\mathrm{CN})_4]^-$ is predicted to have components similar to those of the *trans*-bis(diamine) complex, as exemplified by the close correspondence between the components of $[\mathrm{Pt}(R\text{-pn})(\mathrm{NH_3})_2]^{2+}$ and $[\mathrm{Pt}(R\text{-pn})_2]^{2+}$.[20] This holds clearly from Table I, though the positions of CD components are shifted by larger changes in ligand field for the present case. On further lowering the symmetry to C_{2v}, the $\rightarrow {}^1\mathrm{E}_{1g}$ components under D_{4h} decompose into A and B components, but these splittings are predicted to be small. Thus, the signs of the CD components of $[\mathrm{Co}(R\text{-pn})(\mathrm{CN})_4]^-$ and $[\mathrm{Co}(R\text{-chxn})(\mathrm{CN})_4]^-$ are in agreement with those expected from the empirical rule or regional rule,[1] in which the sign of each CD component is determined by the chirality of the chelate ring, λ. The magnitude of CD ($\Delta\epsilon$) of the monoamine complex is almost half of that of the corresponding diamine complex, as found in the Pt(II) complexes.[20]

An analogous argument is applicable to the CD components of the Fe(II) complexes; namely, the lower wavenumber component has its origin from the $^1\mathrm{A}_{1g} \rightarrow {}^1\mathrm{A}_{2g}$ transition, and the higher wavenumber component arises from the $^1\mathrm{A}_{1g} \rightarrow {}^1\mathrm{E}_{1g}$ transition under D_{4h} symmetry. This supports the postulate that corresponding CD components of isoelectronic and isostructural complexes have the same sign. The magnitude of the positive CD components of the Fe(II) complexes is small compared with the Co(III) complexes, and the ratio of $\Delta\epsilon$ is about 0.5. But the trend is reversed for the negative component, and the magnitude of this component decreases by varying the diamine from R-pn to R-chxn. These results suggest that the magnitude of CD depends on the stereochemistry of the complexes as well as on electronic factors. The change in magnitude of CD with various d^6 complexes has been reported by Ito et al. for *trans*-$[\mathrm{M}(R\text{-pn})_2\mathrm{Cl}_2]^{n+}$, where M represents Co(III), Pd(IV), Pt(IV), and Rh(III).[21] The magnitudes, $\Delta\epsilon$, decrease in the order of Co(III) > Rh(III) > Pd(IV) > Pt(IV). This order indicates that an increase in oxidation number of central metal ions results in a decrease in the magnitude of CD for the first absorption band's components.[1] But the magnitude of CD for the major positive component of Fe(II) complexes is smaller than that of the Co(III) complexes. The observed optical activity is derived from the dissymmetric chelate ring via metal–nitrogen bonds because the CD is associated with a d–d transition. This dependency of the magnitude of CD on d^6 metal ions appears to be associated with the metal–nitrogen bond lengths of these complexes. Bond lengths of these complexes are approximately evaluated from the effective ionic radii of these low-spin metal ions: Fe(II), 0.61; Co(III), 0.53; Rh(III), 0.67; Pt(IV), 0.63 Å.[22] The correlation is in agreement except for Pt(IV).

The CD of the second absorption band also splits into two components for the Co(III) complexes, a small negative and a small positive component in the order of increasing energy. The signs of CD components for the second absorption band have not been studied because almost all Co(III) complexes fail to reveal split components for this region. Splitting of the second absorption band is expected to occur for low-symmetry complexes.

Both complexes showed positive CD at 41 800 and 46 200 cm^{-1} for the MLCT band. This is in agreement with the empirical rule that the charge-transfer (CT) band of the complexes which have chelate rings of λ conformation gives a positive CD absorption in this region.[23,24] The magnitude of CD is smaller for Fe(II) complexes than Co(III) complexes, as discussed for the magnitude of the CD effect of the LF region.

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Registry No. $\mathrm{K[Co(CN)_4}(R\text{-pn})]$, 58410-51-8; $\mathrm{K[Co(CN)_4}(R\text{-chxn})]$, 64784-64-1; $\mathrm{Na_2[Fe(CN)_4}(R\text{-pn})]$, 64784-66-3; $\mathrm{Na_2[Fe(CN)_4}(R\text{-chxn})]$, 64813-42-9; $\mathrm{K_3[Co(CN)_5Br]}$, 14650-10-3.

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Preparation of the Binary Sulfur–Nitrogen Anions $S_3N_3^-$ and $S_4N_5^-$ from Tetrasulfur Tetranitride and Azides and the Vibrational Spectra of $S_3N_3^-$

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The reaction of tetrasulfur tetranitride, S_4N_4, with alkali metal or tetraalkylammonium azides in ethanol produces either the tetrasulfur pentanitride anion, $S_4N_5^-$ (Li^+, Na^+, K^+), the trisulfur trinitride anion, $S_3N_3^-$ (Cs^+, Me_4N^+, Et_4N^+, n-Pr_4N^+, n-Bu_4N^+), or a mixture of $S_4N_5^-$ and $S_3N_3^-$ (Rb^+). Infrared and Raman spectra of the cesium salt suggest a cyclic structure with C_{3v} symmetry for $S_3N_3^-$, which is an "electron-rich aromatic" (10π) system according to earlier postulates for binary sulfur–nitrogen species. The $S_3N_3^-$ anion is also formed from the reaction of excess sodium sulfide with S_4N_4 in ethanol, but $S_4N_5^-$ is produced when excess S_4N_4 is present. The reaction of $Bu_4N^+S_3N_3^-$ with S_4N_4 produces $Bu_4N^+S_4N_5^-$. A mechanism is proposed for the formation of $S_3N_3^-$ and $S_4N_5^-$ in these reactions.

Introduction

Recent interest in the metallic properties and superconductive behavior of polymeric sulfur nitride, $(SN)_x$,[1] has focused attention on binary sulfur–nitrogen compounds. The central character in this chemistry is the intriguing molecule S_4N_4. Reactions of S_4N_4 with different inorganic oxidizing agents have led to the isolation and characterization of a number of binary sulfur–nitrogen cations, e.g., $S_3N_2^+$,[2,3] $S_4N_3^+$,[4] $S_4N_4^{2+}$,[5] $S_5N_5^+$,[6] and $S_6N_4^{2+}$.[7] Such versatile behavior suggests that a wide variety of structural types might also pertain for binary sulfur–nitrogen anions. An indication of this possibility came from the report of the unexpected isolation of a salt of the $S_4N_5^-$ ion[8] and the subsequent structural characterization of this anion by x-ray crystallography.[9] We have recently isolated and characterized the dark blue salt $Bu_4N^+NS_4^-$[10] and later discovered that the reaction of azides with elemental sulfur in hexamethylphosphoramide is a convenient source of the NS_4^- anion.[11] Prompted by the proposed structure for $S_4N_5^-$,[8] we have investigated the reaction of azides of S_4N_4 and found that this reaction provides an easy route to salts of the $S_4N_5^-$ anion[12] or of the novel $S_3N_3^-$ ion.[13] Here we report the full details of these syntheses and of the characterization of $S_3N_3^-$, and we discuss the interrelationship of the $S_3N_3^-$ and $S_4N_5^-$ ions.

Experimental Section

General Procedures. Absolute ethanol was refluxed with magnesium and a crystal of iodine for 4 h and freshly distilled before use. Absolute methanol was distilled from Drierite. Both solvents were stored under N_2 in flame-dried septum-sealed flasks. n-Pentane (Burdick and Jackson) was distilled from CaH_2 and diethyl ether (Mallinckrodt) from $LiAlH_4$. The distillation of solvents, the reactions of azides with S_4N_4, and subsequent handling of $S_3N_3^-$ and $S_4N_5^-$ salts were carried out under N_2 (99.99% purity passed through Ridox and silica gel).

S_4N_4 (mp 179 °C) was prepared according to the literature,[16] recrystallized twice from benzene, and checked for the absence of c-S_8 by mass spectrometry. Sodium azide (Fisher), potassium azide (Eastman), rubidium and cesium azides (Alfa 99.9%), anhydrous lithium and sodium sulfides (Alfa), and trichloroacetyl chloride (Eastman) were used as received. Tetraalkylammonium hydroxides were obtained as solutions in water (R = Et, Pr) or methanol (R = Me, n-Bu) (Eastman). Tetraalkylammonium and lithium azides were prepared by the neutralization of a 10% solution of hydrazoic acid, generated by passing a sodium azide solution over Amberlite IR-120 (H) ion-exchange resin, with the appropriate tetraalkylammonium or lithium hydroxide.[17] The previously described procedure[17] for the purification of these azides was found to be unsatisfactory, and we therefore include a description of our purification procedure for the crude products. Me_4NN_3 was slurried twice with acetonitrile, and the white solid residue, after filtration, was dissolved in the minimum amount of methanol and precipitated with diethyl ether. Et_4NN_3 was dissolved in the minimum amount of acetonitrile and precipitated with diethyl ether (twice). n-Pr_4NN_3 was dissolved in the minimum amount of absolute ethanol and precipitated with diethyl ether (twice). Crude n-Bu_4NN_3 was obtained as a sticky solid and was slurried twice with diethyl ether/acetone (150:5 mL) to give a white powder after filtration. The azides were dried in an Abderhalden pistol at ca. 65 °C and 10^{-2} mmHg (Me_4N^+, Et_4N^+, n-Pr_4N^+) and at 25 °C (Li^+, n-Bu_4N^+) and were then found to be analytically pure (Table I).

Instrumentation. Infrared spectra (4000–250 cm^{-1}) were recorded as Nujol mulls (CsI optics) on a Perkin-Elmer 467 spectrophotometer, and far-infrared spectra (665–40 cm^{-1}, polyethylene windows) were measured using a Digilab FTS 16 instrument. Raman spectra were obtained on a sample of $Cs^+S_3N_3^-$ in a capillary tube using an argon laser operating at 514.5 nm and a Jarrel-Ash spectrophotometer. Mass spectra were recorded on a Varian CH5 instrument operating at 70 eV. UV-visible spectra were recorded in a 1-cm Airless-ware cell on a Cary 15 spectrophotometer. Microanalyses were performed by Alfred Bernhardt, Mikroanalytisches Laboratorium, Müllheim, West Germany.

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