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Anionic Bridging Ligands: Thiocyanato- and Selenocyanato-Bridged Pentacyanoferrate Dimers and Their Mixed-Valence Properties

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Thiocyanato- and selenocyanato-bridged mixed-valence pentacyanoferrate dimers have been synthesized and characterized by various physicochemical measurements. The $Fe^{II}Fe^{III}$ mixed-valence complexes are stabilized well against disproportionation as shown by their comproportionation constants ($K_c = 1474$ for the SCN^--bridged dimer and 2399 for the $SeCN^-$-bridged dimer). According to our analysis the overall stability of the mixed-valence species over that of isovalent ones has major contributions from the Coulombic factors and electron delocalization effects in anionic-ligand-bridged mixed-valence dimers.

Introduction

The syntheses of ligand-bridged binuclear mixed-valence complexes of transition metals have stimulated a great deal of interest in the past two decades.[1-4] These discrete, relatively simple representative units serve as models and starting points for understanding the otherwise complex electron transmission phenomena through chemical and biological systems.[5-8] Large numbers of robust mixed-valence compounds have been synthesized and studied by using intervalence transfer (IT) band arising from optically induced charge transfer between metal centers through the bridging group. The theoretical treatment of IT bands has been given by Hush,[9,10] by Piepho, Krausz, and Schatz,[11,12] and by Ondrechen with a three-site model that includes explicitly the bridging species.[13,14] The Hush treatment concludes that information on the extent of communication between metal centers could be obtained from the intensity of the IT band.

The feasibility of using thiocyanate ion as a bridging ligand in such systems has been established recently.[15] The thiocyanato group, in spite of its intrinsic asymmetry, has been found to mediate a valence delocalization (class III behavior in the Robin and Day[16] sense), possibly through a π^* orbital, between two $[Ru(NH_3)_5]^{n+}$ (n = 2 or 3) units. Thiocyanato-mediated valence delocalization is in contrast to situations where other intrinsically asymmetric ligands are involved, such as cyanide ion[17] (class II behavior in the Robin and Day sense).

Further, the behavior of the mixed-valence compounds of pentacyanoferrates reported until now seems paradoxical. The bridging ligands that impart a fairly good amount of stability to $[Ru(NH_3)_5]^{2+/3+}$ systems through the $M(d\pi)-L(\pi^*)-M(d\pi)$ interaction seems to impart lesser stability to $[Fe(CN)_5]^{3-/2-}$ systems (cf. Table I).[18] This led us to combine the pentacyanoferrate moieties with thiocyanato and selenocyanato ions and generate the mixed-valence compounds. The results obtained are interpreted in terms of the relative stability of the mixed-valence compounds over that of the isovalent ones.

Experimental Section

Materials. All the reagents used were of chemically pure or AnalaR grade. Doubly distilled water was used throughout. Sodium amminepentacyanoferrate(II) trihydrate was prepared by a standard procedure,[19] purified,[20] and then dried to constant weight over KOH, which absorbs alcohol but not ammonia.[21] A strong and sharp signal in the IR spectrum at 1245 cm^{-1} was used as a diagnostic for the presence of the ammonia molecule.[22] Commercial grade sodium thiocyanate, potassium selenocyanate (Fluka AG), tetraphenylphosphonium chloride (Aldrich), and rubidium chloride (S. D. Chemicals) were used as such.

Dowex 50W-X8 (200–400 μm) in the hydrogen form and Dowex 1-X8 (100–200 μm) in the chloride form, Sephadex G-10 (40–120 μm), Sephadex G-25 (50–150 μm), and Sephadex LH-20 (25–100 μm) (Pharmacia Fine Chemicals) were used for various chromatographic studies.

Table I. Comproportionation Constant Values for Ligand-Bridged Pentaammineruthenium and Pentacyanoferrate Mixed-Valence Dimers

L^a	K_c-($Ru^{II}Ru^{III}L$)	K_c-($Fe^{II}Fe^{III}L$)	L^a	K_c-($Ru^{II}Ru^{III}L$)	K_c-($Fe^{II}Fe^{III}L$)
pyz	4×10^6	50	BPE	14	4
4,4'-bpy	24	4	CN^-		5

[a] Abbreviations: pyz, pyrazine; 4,4'-bpy, 4,4'-bipyridine; BPE, *trans*-1,2-bis(4-pyridyl)ethylene.

Preparations. (a) (μ-Thiocyanato)- or (μ-Selenocyanato)bis[pentacyanoferrate(III)]. A typical reaction to prepare the binuclear complexes was carried out as follows: Air was stirred into the solution of sodium amminepentacyanoferrate(II) trihydrate (ca. 2 mmol) in 15 mL of water for 15 min followed by the addition of 5 mL of a solution of sodium thiocyanate or potassium selenocyanate (ca. 1 mmol). The color of the solution immediately changed to green. Air was bubbled overnight through the resulting mixture, effecting the intensification of the green color. The stirring of the solution was continued until dark yellow or red-brown components of the solution disappeared. The solution was filtered through a fine-porosity sintered crucible and was sorbed on to a column of Sephadex G-10 (40 × 2 cm). The compounds were eluted with water. With a slow enough elution rate, clear separation of two bands was noticed. The large greenish yellow first band and the blue second band (in smaller amounts) were eluted separately and concentrated at room temperature (even at 50 °C the compounds decomposed to give a dark blue, insoluble polymeric product). An excess of a methanol and acetone mixture (4:1, v/v) was added to the concentrates with stirring. The precipitated $Na_5[Fe(CN)_5NCSFe(CN)_5]\cdot xH_2O$ and $Na_3[Fe(CN)_5NCS]\cdot xH_2O$ or the corresponding sodium and potassium salts of the selenocyanate analogues were filtered respectively from the first and second bands. They were washed extensively with methanol and

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(1) Taube, H. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 329.
(2) Richardson, D. E.; Taube, H. *Coord. Chem. Rev.* **1984**, *60*, 107.
(3) *Mixed Valence Compounds*; Brown, D. B., Ed.; Reidel: Dordrecht, Holland, 1980.
(4) Meyer, T.J. In *Progress in Inorganic Chemistry*; Wiley: New York, 1983; Vol. 30.
(5) Guarr, T.; McLendon, G. *Coord. Chem. Rev.* **1985**, *68*, 1.
(6) Gray, H. B. *Chem. Soc. Rev.* **1986**, *15*, 17.
(7) McLendon, G.; Guarr, T.; McGuire, M.; Simolo, K.; Strauch, S.; Taylor, K. *Coord. Chem. Rev.* **1985**, *64*, 113.
(8) Isied, S. S.; Vassilian, A.; Magnuson, R. H.; Schwarz, H. A. *J. Am. Chem. Soc.* **1985**, *107*, 7432.
(9) Hush, N. S. In *Progress in Inorganic Chemistry*; Wiley: New York, 1967; Vol. 8, p 391.
(10) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.
(11) Piepho, S. B.; Krausz, E. R.; Schatz, P. N. *J. Am. Chem. Soc.* **1978**, *100*, 2996.
(12) Schatz, P. N. In ref 3, p 115.
(13) Ondrechen, M. J.; Ko, J.; Root, L. J. *J. Phys. Chem.* **1984**, *88*, 5919.
(14) Ko, J.; Ondrechen, M. J. *Chem. Phys. Lett.* **1984**, *112*, 507.
(15) Palaniappan, V.; Yadav, S. K. S.; Agarwala, U. C. *Polyhedron* **1985**, *4*, 1457.
(16) Robin, M. B.; day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.
(17) Glauser, R.; Hauser, U.; Herren, F.; Ludi, A.; Roder, P.; Schmidt, E.; Siegnhaler, H.; Wenk, F. *J. Am. Chem. Soc.* **1973**, *95*, 8457.
(18) Michiels, L. P., personal communication.
(19) Bruauer, G. *Handbook of Preparative Inorganic Chemistry*, 2nd ed.; Academic: New York, 1965; p 1511.
(20) Jwo, J. J.; Haim, A. *J. Am. Chem. Soc.* **1976**, *98*, 1172.
(21) Michiels, L. P.; Kolks, G.; Nesbitt, E. R.; Dimauro, P. T.; Krichner, R. M.; Waszczak, J. V. *Inorg. Chim. Acta* **1985**, *100*, 211.
(22) Herington, E. F.; Kynaston, W. *J. Chem. Soc.* **1955**, 3555.

Table II. Electrochemical Data[a] for the NCX-Bridged Dimers

compd	E_1/mV	ΔE_1/mV[b,c]	E_2/mV	ΔE_2/mV[c]	K_c	$\Delta G°_{tot}$/kcal mol^{-1} [d]	ΔE/mV[e]
$[Fe(CN)_5NCSFe(CN)_5]^{n-}$ [f]	175.0	150	362.5	75	1474	1.771	187.5
$[Fe(CN)_5NCSeFe(CN)_5]^{n-}$ [f]	162.5	175	362.5	75	2399	1.916	200.0
$[Ru(NH_3)_5NCSRu(NH_3)_5]^{n+}$ [g]	325.0		538.0	75			213.0

[a] Potentials are referred to the SCE. [b] Irreversible process. [c] $\Delta E_{1,2} = E_{p,a} - E_{p,c}$. [d] $\Delta G°_{tot}$ values were calculated by using the equation $\Delta G° = -RT \ln (K_c/4)$, where 4 is the statistical contribution. [e] Separation between two redox stages; $\Delta E = E_2 - E_1$. [f] Rubidium salts. [g] From ref 15.

acetone and dried over calcium chloride; yields 60% and 10–15%, respectively, from the first and second bands for the thiocyanate case and 70–80% and 5–10%, respectively, from the first and second bands for the selenocyanate case.

The acid salts of the compounds $[Fe(CN)_5NCXFe(CN)_5]^{5-}$ (X = S, Se) were prepared by passing the respective solutions through the cation exchanger in the hydrogen cycle. The deep blue acid salt was eluted with water and was neutralized with appropriate base to pH 7, and on removal of the solvent water at low pressure, the solution yielded the salts of the corresponding cations. (Neutralization with sodium carbonate, potassium carbonate, tetraethylammonium hydroxide, and tetrabutylammonium hydroxide yielded the corresponding sodium, potassium, tetraethylammonium, and tetrabutylammonium salts, respectively.) The salts were washed extensively with acetone and dried under vacuum over calcium chloride.

Tetraphenylphosphonium and rubidium salts of the dimeric anions were also prepared. An excess of $(C_6H_5)_4PCl$ in 20 mL of a 1:2 (v/v) mixture of water and ethanol was added to an aqueous solution of the sodium salt of the dimer. Slow evaporation over a period of a few days yielded green microcrystalline tetraphenylphosphonium salts of the dimeric compounds. Anal. Calcd for $(PPh_4)_5[Fe(CN)_5NCSFe(CN)_5]\cdot 8H_2O$: C, 69.28; H, 5.11; N, 6.79; S, 1.41; Fe, 4.94. Found: C, 69.48; H, 5.16; N, 6.06; S, 2.01; Fe, 4.55. Calcd for $(PPh_4)_5[Fe(CN)_5NCSeFe(CN)_5]\cdot 6H_2O$: C, 68.95; H, 4.91; N, 6.75; Se, 3.47; Fe, 4.91. Found: C, 69.10; H, 5.11; N, 6.56; Se, 3.45; Fe, 4.80.

The procedure to prepare the rubidium salt was the same as that given for the $(PPh_4)^+$ salt except that an aqueous solution of RbCl was used in place of PPh_4Cl. The compounds were washed with acetone and ether and dried over calcium chloride. More of the rubidium salt can be precipitated from the mother liquor by adding an excess of a methanol and ether mixture with stirring. Anal. Calcd for $Rb_5[Fe(CN)_5SCNFe(CN)_5]\cdot H_2O$: C, 15.06; H, 0.22; N, 17.58; S, 3.65; Fe, 12.79. Found: C, 15.04; H, 1.71; N, 17.50; S, 3.60; Fe, 12.45. Calcd for $Rb_5[Fe(CN)_5SeCNFe(CN)_5]\cdot 2H_2O$: C, 14.03; H, 0.43; N, 16.37; Se, 8.39; Fe, 11.90. Found: C, 13.68; H, 1.84; N, 16.41; Se, 8.01; Fe, 11.55.

(b) (μ-Thiocyanato)- or (μ-Selenocyanato)bis[pentacyanoferrate(II)]. Sodium amminepentacyanoferrate(II) trihydrate (ca. 2 mmol) and sodium thiocyanate or potassium selenocyanate (ca. 1 mmol) were mixed simultaneously in degassed water (15–20 mL under a dinitrogen atmosphere. The solution was stirred for about 10 h. The resulting pale yellow solution was filtered into an excess of a methanol and acetone mixture (4:1, v/v) with stirring. The bright yellow precipitate obtained was filtered, washed extensively with acetone, and dried under vacuum. The compound when passed through a Sephadex G-10 column showed a large yellow band and a smaller brown band, which was discarded. The yellow compound had a tendency to deliquesce in the atmosphere and probably underwent oxidation to yield a mixture of the mixed-valence and completely oxidized products.[18]

(c) (μ-Thiocyanato)- or (μ-Selenocyanato)bis[pentacyanoferrate(II,-III)]. These species were generated in situ by the reduction of $[Fe(CN)_5NCXFe(CN)_5]^{5-}$ (X = S, Se) species with stoichiometric amounts of $K_4[Fe(CN)_6]$, hydroquinone, or aqueous Cr^{2+} solution. Considerable amounts of solid compound were also isolated by Sephadex column chromatography from a solution containing a 1:1 (stoichiometric) mixture of $Na_5[Fe(CN)_5NCXFe(CN)_5]$ and the product of the reaction carried out by procedure b. The aqueous solution of the mixture was sorbed onto a column of Sephadex G-25, and with a slow enough elution rate with water as the eluting solution, three bands were seen. The middle one when added to an excess of a methanol and acetone mixture (4:1, v/v) yielded the desired product. This was washed with acetone and dried under vacuum in the dark. Anal. Calcd for $Rb_6[Fe(CN)_5SCNFe(CN)_5]\cdot 5H_2O$: C, 12.78; H, 0.97; N, 14.91. Found: C, 12.36; H, 1.84; N, 14.95. Calcd for $Rb_6[Fe(CN)_5SeCNFe(CN)_5]\cdot 4H_2O$: C, 12.43; H, 0.75; N, 14.50. Found: C, 12.25; H, 1.69; N, 14.21.

All the compounds have a tendency to absorb moisture extensively from the atmosphere. Hence, they were generally stored over calcium chloride in a vacuum desiccator.

Physicochemical Measurements. Details of the physicochemical methods are given elsewhere.[23] Near-infrared spectra were recorded with solvents that were dried before use on a Cary 17D spectrophotometer. Mössbauer spectra were obtained by using a constant-acceleration drive with a 15-mCi ^{57}Co source obtained from New England Nuclear Co. The data were stored in a Canberra S-80 multichannel analyzer. The experimental data were least-squares fitted for Lorentzian shapes by using the MOSFIT program.[67] The Mössbauer spectrometer was calibrated by using natural iron. Magnetic measurements were done on a Gouy balance using $Hg[Co(NCS)_4]$ as the standard. The cyclic voltammetric experiments were performed with a three-electrode potentiostatic circuit, a MPI Model MP1042 voltammetry controller, and a Plotamatic MF 715 X-Y recorder. A Beckman Pt electrode, a Pt-wire counter electrode, and saturated calomel electrode constitute the three-electrode assembly. Potassium nitrate was used as the supporting electrolyte. Junction potentials were eliminated by using a salt bridge consisting of the same concentration of base electrolyte as that of the bulk solution, and the bridge was positioned between the bulk test solution and the reference electrode. All potentials are quoted with respect to the SCE.

Results

Binuclear Complexes. The completely reduced (22) dimer [(22), (23), and (33) represent the three different stages of oxidation states for the dimers $[Fe(CN)_5NCXFe(CN)_5]^{n-}$ where X = S and Se and n = 7, 6, and 5] was obtained when the reactants were simultaneously mixed in aqueous solution. In fact, this was an exclusive product when the reaction was carried out in degassed water under a dinitrogen atmosphere. If air was bubbled instead of dinitrogen, the reaction yielded all three of the (22), (23), and (33) species. The (22) species that is formed is believed to be partially oxidized to (23) and (33) species. Also, remaining (22) might have reacted with (33) in solution to give the mixed-valence (23) species:

$$(22) + (33) \overset{K_c}{\rightleftharpoons} 2(23) \qquad (1)$$

This is a viable route to prepare the mixed-valence species as seen from the values of the comproportionation quotient (cf. Table II). A delay of 10–20 min in the addition of NCX^- ion to the aerated aqueous solution of $Na_3[Fe(CN)_5NH_3]$ yielded exclusively the oxidized species (33) with a small amount of monomeric $[Fe(CN)_5NCS]^{3-}$, which was identified by its electronic spectrum.[24]

All the compounds except the Rb salts showed a strong tendency to absorb atmospheric moisture and deliquesce with probable decomposition. As a result, it is very difficult to obtain consistent and satisfactory microanalytical results and especially in the case of the (22) dimer we could not get satisfactorily reproducible results.

Aging of the (22) solution in the atmosphere led to the properties of the (33) species to a considerable extent. A deformed band in the near-IR region having somewhat lower intensity (vide supra) was observed. Hence it was concluded that (22) compounds are unstable and are oxidized to (23) and (33) species in the course of time. The instability of (22) species can be attributed to the smaller π-acidities of the NCX^- ions compared to those of cyanide ion or pyrazine. Due to this intrinsic instability of the (22) dimer, the reduction of (33) species seems to be a better pathway to synthesize the mixed-valence ions rather than the oxidation of (22) species. Reduction of (33) species with hydroquinone, $K_4[Fe(CN)_6]$, and Cr^{2+} as the reducing agents yielded the mixed-valence species and was found to have two steps of reduction corresponding to the molar stoichiometries 1:1 and 1:2 of the (33) species and the reducing agent, resulting in blue and light yellow solutions.[25]

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(23) Palaniappan, V.; Agarwala, U. C. *Inorg. Chem.* **1986**, *25*, 4064.

(24) Gutterman, D. F.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 1727.

Table III. Infrared Spectral Data (cm^{-1}) and Their Assignments for $[Fe(CN)_5NCXFe(CN)_5]^{n-}$ [a,g]

$[Fe(CN)_5NCXFe(CN)_5]^{5-}$		$[Fe(CN)_5NCXFe(CN)_5]^{6-}$		$[Fe(CN)_5NCXFe(CN)_5]^{7-}$ [b]		
X = S[c]	X = Se[d]	X = S[e]	X = Se[e]	X = S[f]	X = Se[f]	assignts
2125 (s)	2140 (s)	2130 (s)	2120 (s)	2075 (s)	2060 (s)	ν(CN) of NCX^-
2100 (vs)	2090 (vs)	2090 (vs)	2085 (vs)	...	...	ν(CN) of $[Fe^{III}(CN)_5]^{n-}$
...	...	2055 (s, sh)	2050 (s, sh)	2050 (vs)	2050 (vs)	ν(CN) of $[Fe^{II}(CN)_5)]^{n-}$
730	580	750	575	730	...	ν(CX) of NCX^-
460	420	460	415	...	...	δ(NCX) of NCX^-
530	520	590	575	620	...	δ(FeCN)
		530 (s, sh)	525 (s, sh)			
385	380	405	405	410	...	ν(FeC)

[a] Unless otherwise stated, the spectra were recorded in KBr and CsI disks. [b] Recorded in a Nujol mull. [c] Tetraphenylphosphonium salt. [d] Tetraethylammonium salt. [e] Rubidium salts. [f] Sodium salts. [g] Water of crystallization appeared as two characteristic peaks at around 3450 and 1640 cm^{-1}. Peaks due to various cations such as PPh_4^+, NEt_4^+, NBu_4^+, etc. were obtained at their characteristic positions and are not given here.

Table IV. Electronic Spectral Data[a] for the Thiocyanato-Bridged Compounds $[Fe(CN)_5NCSFe(CN)_5]^{n-}$

compd	λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})	assignt	ref
$n = 7$[b]	395 (sh)	...	this work
	325 (sh)	...	
	285 (sh)	...	
	225 (vs)	...	
$n = 6$[c]	1300 (670)	IT	this work
	770 (sh)	...	
	393 (1420)	LF, π(NCS)–dπ(Fe)	
	355 (1420)	σ(CN)–dπ(Fe)	
	325 (1700)	...	
	280 (2150)	π(CN)–dπ(Fe)	
	245 (2375)	π(CN)–dπ(Fe)	
	210 (10 160)	IL, NCS^-	
$n = 5$[d]	715 (1600)	2π(NCS)–dπ(Fe)	this work
	412 (sh, 1700)	LF, σ(CN)–dπ(Fe)	
	405 (1800)	π(NCS)–dπ(Fe)	
	320 (sh)	LF	
	295 (4430)	IL, NCS^-	
	280 (4210)	π(CN)–dπ(Fe)	
	250 (5400)	π(CN)–dπ(Fe)	
	215 (vs)	IL, NCS^-	
$[Fe(CN)_5NCS]^{3-}$	521 (3600)	2π(NCS)–dπ(Fe)	24
	395 (520)	LF	
	350 (995)	σ(CN)–dπ(Fe)	
	323 (1090)	π(CN)–dπ(Fe)	
	300 (1360)	LF	
	270 (2130)	π(CN)–dπ(Fe)	
	260 (2280)	π(CN)–dπ(Fe)	

[a] Spectra were recorded in water solutions. [b] Sodium salt. [c] Rubidium salt. [d] Tetrabutylammonium salt.

Table V. Electronic Spectral Data[a] for the Selenocyanate-Bridged Compounds $[Fe(CN)_5NCSeFe(CN)_5]^{n-}$

compd	λ_{max}/nm (ϵ_{max}/M^{-1} cm^{-1})	assignt	ref
$n = 7$[c]	420 (s, sh)	...	this work
	330 (sh)	...	
	285 (-)	...	
	245 (-)	...	
$n = 6$[b]	1264 (730)	IT	this work
	730 (sh)	...	
	398 (1380)	LF, π(NCSe)–dπ(Fe)	
	318 (1640)	σ(CN)–dπ(Fe)	
	295 (2180)	π(CN)–dπ(Fe)	
	275 (2520)		
	240 (3330)		
	213 (12 650)	IL, $NCSe^-$	
$n = 5$[c]	690 (1750)	2π(NCSe)–dπ(Fe)	this work
	410 (sh)	LF, σ(CN)–dπ(Fe)	
	396 (2250)	π(NCSe)–dπ(Fe)	
	320 (sh)	LF	
	290 (4100)	IL, $NCSe^-$ ion	
	248 (4510)	π(CN)–dπ(Fe)	
	220 (vs)	IL, $NCSe^-$	
$[Fe(CN)_5NCSe]^{3-}$	598 (2180)	2π(NCSe)–dπ(Fe)	24
	397 (595)	LF	
	353 (870)	σ(CN)–dπ(Fe)	
	323 (1150)	π(CN)–dπ(Fe)	
	275 (3226)	π(CN)–dπ(Fe)	
$[Fe(CN)_5CN\text{-}Fe(CN)_4NH_3]^{4-}$	625 (-)		21

[a] Spectra recorded in water solutions. [b] Rubidium salt. [c] Sodium salt.

Table VI. Solvent-Dependent Near-IR Spectral Data for $[Fe(CN)_5SeCNFe(CN)_5]^{6-}$ [a,d]

solvent	$(1/n^2) - (1/D)$[b]	ν_{max}(IT)/nm	ϵ_{max}/M^{-1} cm^{-1}
water	0.551	1264	730
dimethylformamide (DMF)	0.464	1278	
dimethyl sulfoxide (DMSO)	0.437	1290	
potassium bromide disk		1340	
perchloric acid (60%)		*c*	

[a] Further solvent-dependent studies are in progress. [b] Taken from: Koppel, I. A.; Palm, V. A. In *Advances in Linear Free Energy Relationships*; Chapman, N. B., Shorter, J., Eds.; Plenum: London, 1972; pp 254–258. [c] Showed a broad band at somewhat higher energies at around 970 nm. The color of the sample solution changed to dark blue, indicating protonation of the cyanide groups. [d] Rubidium salts.

The compositions of the (33) species in the cases of both thiocyanate and selenocyanate were established by Job's method[26] using aqueous solutions of the reactants $Na_3[Fe(CN)_5NH_3]\cdot 3H_2O$ and NCX^- ion. From the Job plots it was concluded that the species absorbing at 740 and 690 nm (for the $SeCN^-$ ion) contains $[Fe(CN)_5]^{2-}$ and NCX^- ion in a 2:1 molar ratio.[27] The microanalytical data for the compounds were consistent with the compositions.

Infrared spectroscopy provides a simpler method to establish the oxidation states of the pentacyanoferrate moieties. The cyanide stretching frequencies of iron(II) cyanides fall in the range 2070–2030 cm^{-1}, whereas the range for iron(III) cyanides is 2130–2090 cm^{-1}.[28] The (33) and (22) compounds exhibited two bands in the cyanide stretching region corresponding to bridging NCX and the pentacyanoferrate moieties. ν(CN) of the NCX bridge for (22) species was observed at markedly lower energy compared to that of the (33) species (cf. Table III). This might be due to comparatively larger π-donation in (22) species to the LUMO of the NCX^- ion, a π^* orbital, which is antibonding with respect to both C–N and C–X bonds[29] (*vide supra*). The bands

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(25) The pale yellow solution showed an electronic spectrum, which resembled that of the (22) species, in the case of selenocyanate, and for thiocyanate the resemblance was not complete.

(26) The reaction was very slow at a 10^{-4} M concentration level of the reactants. Hence, solutions of 10^{-1} M concentration were used. The mixture was allowed to equilibrate in the dark under air. Portions of these solutions diluted to 10^{-4} M concentration were scanned from time to time, and the limiting values of absorption at the appropriate wavelengths were obtained.

(27) Limiting values of absorption were plotted as a function of F [$F = [Fe(II)]_{init}/([Fe(II)]_{init} + [NCX^-]_{init})$, Fe(II) denoting $[Fe(CN)_5NH_3]^{3-}$]. The plots displayed a sharp maximum at $F = 0.66$ for the SCN^- ion and $F = 0.68$ for the $SeCN^-$ ion.

(28) Dows, D. A.; Wilmarth, W. K.; Haim, A. *J. Inorg. Nucl. Chem.* **1961**, *21*, 33.

Table VII. Characteristic Parameters Calculated from IT Bands and Hush Formulas

compd	$\tilde{\nu}_{IT}$/ cm^{-1}	ϵ_{max}/ $M^{-1}\ cm^{-1}$	$\Delta\tilde{\nu}$(exptl)/ cm^{-1}	$\Delta\tilde{\nu}$(calcd)/ $cm^{-1\,a}$	$10^2 f^a$	D/Å^a	$10^{10}\lvert M\rvert$/ Å esu^a	$10^3\alpha^a$
$[Fe(CN)_5NCSFe(CN)_5]^{6-\,b}$	7692	670	3553	4215	1.095	0.36	1.74	5.3
$[Fe(CN)_5NCSeFe(CN)_5]^{6-\,b}$	7911	730	3086	4275	1.036	0.35	1.67	5.0

^{a}Calculated by using "Hush formulas". ^{b}Rubidium salts.

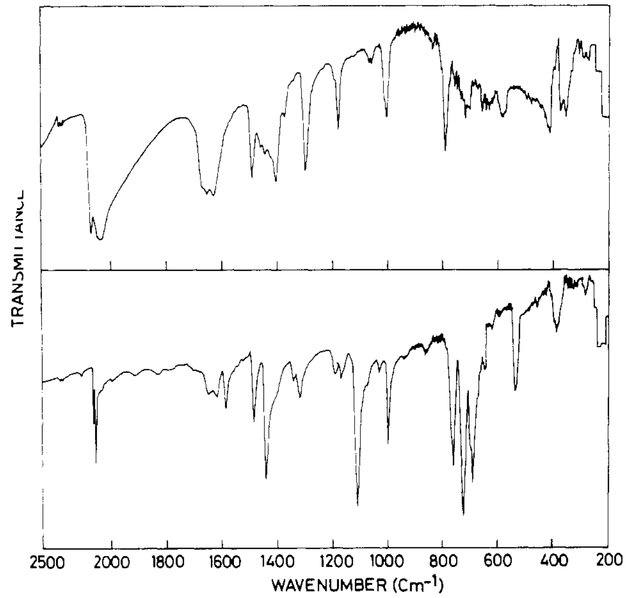

Figure 1. Infrared spectra of the representative compounds: (bottom) $(PPh_4)_5[Fe(CN)_5NCSFe(CN)_5]\cdot xH_2O$; (top) $[(C_2H_5)_4N]_6[Fe(CN)_5NCSFe(CN)_5]\cdot xH_2O$.

due to ν(CX), δ(NCX), δ(FeCN), and ν(FeC) modes of vibrations were also obtained in their respective characteristic frequency ranges and are given in Table III.

The (23) species exhibited ν(CN) bands corresponding to the bridged NCX moiety and to the pentacyanoferrates in +2 and +3 oxidation states. The bands due to ν(CN) of the NCX moiety and $[Fe(CN)_5]^{3-}$ were observed as overlapping bands whose half-width was abnormally large and could be resolved into two bands having absorbances at around 2050 and 2085 cm^{-1}. Similarly the band due to δ(FeCN) was observed at two different frequencies characteristic of $[Fe(CN)_5]^{3-}$ and $[Fe(CN)_5]^{2-}$ units (Figure 1). Infrared spectra of the compounds with different cations did not show any marked difference (±5 cm^{-1}) in the positions of the various bands thus far discussed.

The essential features of the electronic spectra of the dinuclear complexes obtained by dissolving the solid in aqueous solution are given in Tables IV and V and were identical with those recorded for the species generated directly in solution (Figure 2).

The electronic spectra of the pale yellow aqueous solution of the (22) species exhibited a host of shoulders below 400 nm (cf. Figure 2), and accurate values for their extinction coefficients could not be determined. The spectra of (33) species exhibited a band at around 715 nm (690 nm in the case of the SeCN$^-$ ion) whose position varied considerably with the change in the countercation.[30] Another band was observed at around 400 nm, which exhibited a low-energy shoulder of almost equal intensity. This band, arising due to a ligand field transition, in the corresponding monomeric compounds (cf. Tables IV and V) showed a marked increase in intensity, the reason for which could not be ascertained as similar higher intensity bands were observed in other pentacyanoferrate dimers having different bridging ligands.[21,31] A tentative explanation could be that this band might involve contributions from other charge-transfer transitions, such as σ (CN) → t_{2g} (Fe).[21] The bands at around 700 nm in the (33) species can be attributed to π (NCX) → t_{2g} (Fe) (LMCT) charge transfer.[24] The energies of the highest occupied π^* orbitals of NCS$^-$, NCSe$^-$, and CN$^-$ ions vary as NCS$^-$ > NCSe$^-$ > CN$^-$.[32,33] Assuming that the t_{2g} (Fe) acceptor orbital is not perturbed very much by the π-donation from the ligands, the energies of the CT band should vary as NCS$^-$ < NCSe$^-$ < CN$^-$. The observed behavior parallels this (cf. Tables IV and V). Also, the intensity of this band is reduced approximately by half in the case of dimeric compounds compared to that of the corresponding monomeric compounds. This is a corroborative observation for the nature of the band, i.e., LMCT.

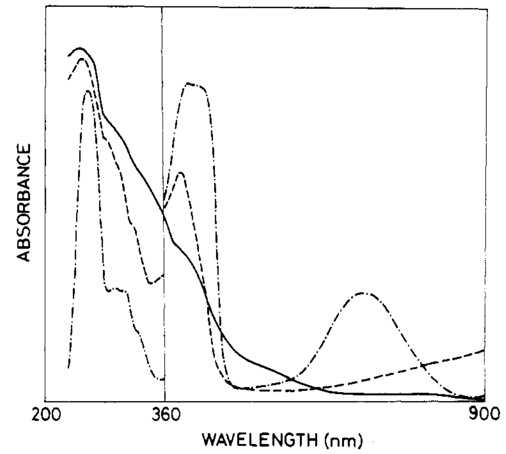

Figure 2. Electronic spectra of the selenocyanato-bridged pentacyanoferrate dimers: (—) (22) dimer; (- - -) (23) dimer; (-·-) (33) dimer.

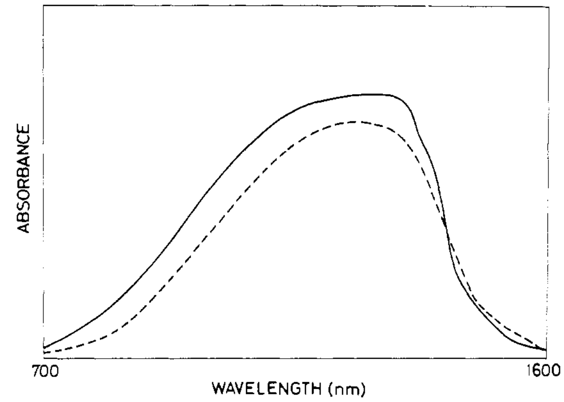

Figure 3. Near-IR spectra of the mixed-valence pentacyanoferrate dimers: (—) thiocyanato-bridged dimer; (- - -) selenocyanato-bridged dimer.

The (23) compounds exhibited a broad and fairly intense asymmetric band (Figure 3) in the near-IR region at around 1300 and 1264 nm for the thiocyanato- and selenocyanato-bridged compounds, respectively. This band can be attributed to intervalence transfer (IT):

$$(23) \xrightarrow{h\nu} (23) \qquad (2)$$

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(29) Rabalais, J. W.; McDonald, J. M.; Sherr, V.; McGlynn, S. P. M. *Chem. Rev.* **1971**, *71*, 73.

(30) An insoluble light blue silver salt of the (33) compound was synthesized, the reflectance spectrum of which showed the CT band at around 880 nm. The Rb salt showed the band at around 740 nm. Further work regarding this aspect is under progress.

(31) Felix, F.; Ludi, A. *Inorg. Chem.* **1978**, *17*, 1782.

(32) Norbury, A. H. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 231.

(33) We assume that the HOMO of the CN$^-$ ion (π^b level) is around −14 eV, from the ionization potential of the HCN molecule (~14 eV) (see ref 56b).

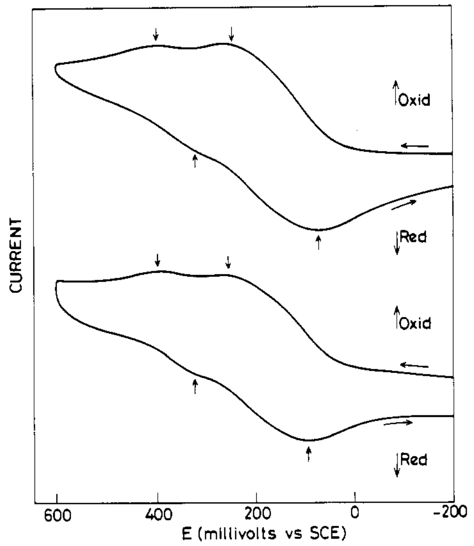


Figure 4. Cyclic voltammograms of the (23) dimers in water solution: (bottom) thiocyanato-bridged dimer; (top) selenocyanato-bridged dimer. The scan rate is 100 mV s^{-1}. Values of $E_{1/2}$ and ΔE for $K_4[Fe(CN)_6]$ under the same conditions are 237.5 and 75 mV, respectively.

Ignoring the asymmetry[65] of the bridging ligand and assuming a linear bridge, the conceptual model proposed by Hush[9,10] for class II mixed-valence compounds can be applied to calculate the mixing coefficient (α). For a symmetrical one-electron transfer, the absorption maximum and the band width can be calculated from each other. In the high-temperature limit at 300 K

$$\nu_{max} = (\Delta\nu_{1/2})^2/2310 \tag{3}$$

ν_{max} and $\Delta\nu_{1/2}$ are in cm^{-1}. Values for the oscillator strength of the IT band (f), the dipole strength (D), the transition dipole moment ($|M|$), and the mixing coefficient (α) were calculated by using eq 4–7 derived by Hush and are given in Table VII. A

$$f = (4.6 \times 10^{-9})\epsilon_{max}\,\Delta\nu_{1/2} \tag{4}$$

$$D = (f/(1.085 \times 10^{-5})\nu)^{1/2} \tag{5}$$

$$|M| = (4.803 \times 10^{-10})D \tag{6}$$

$$\alpha = Dr^{-1} \tag{7}$$

value of 7 Å was chosen for the distance between the two metal centers.[34]

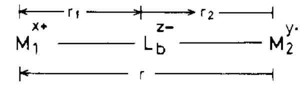
The cyclic voltammograms of the NCX-bridged dimers (Figure 4) were recorded in water with potassium nitrate as the supporting electrolyte. The results are given in Table II. The compounds exhibited two waves corresponding to the two-step oxidation of (22) species. The comproportionation quotients (eq 1) and the stability per mole of the mixed-valence species with respect to the isovalent ones were also calculated. The interesting feature to note is the separation of the two redox stages by 0.1875 and 0.2 V for the thiocyanato- and the selenocyanato-bridged dimers, respectively. The less frequently available Mössbauer data[21,35-37] for the ligand-bridged pentacyanoferrate dimers prompted us to carry out the Mössbauer studies on these compounds. The Mössbauer spectra for the (33) and (23) compounds were recorded at room temperature with polycrystalline samples. The values for the isomer shift, quadrupole splitting parameter, and line width were obtained by a least-squares fit of the experimental spectrum for Lorentzian line shapes. The numerical values are given in Table VIII. Though the isomer shift values of the iron centers in different oxidation states are in an acceptable range with the previously reported values,[21,37] there seems to be a discrepancy in the values for quadrupole splitting parameters, especially in (33) species. These (33) compounds exhibited markedly lower values for ΔE_Q. A probable and tentative explanation is that the electric field gradient (q) created by the NCX$^-$ ligands on the two iron centers that are bridged might be symmetric and approximately equal, resulting in the near-equivalence of the iron sites and hence lowering of the ΔE_Q values.[38] The (23) compounds exhibited a pair of doublets corresponding to different iron centers in +2 and +3 oxidation states. The broad line observed in the spectrum having δ = −0.121 mm s^{-1} could be attributed to a decomposition product, as seen from the change in color of the samples after the Mössbauer measurements. The lower intensity of this peak in the SeCN dimer compared to that of the SCN dimer may be understood in terms of the lesser stability of the SCN dimer as evident from the K_c values.

Table VIII. Mössbauer Data

compd	δ/mm s^{-1} [a]	ΔE_Q/mm s^{-1}	Γ/mm s^{-1}
$Fe^{III}NCSFe^{III}$	−0.126	0.134	0.142
$Fe^{III}NCSeFe^{III}$	−0.122	0.0[b]	0.176
$Fe^{III}NCSFe^{II}$	−0.121	0.0	
	−0.061	1.017	0.168
	−0.120	2.024	0.231
$Fe^{III}NCSeFe^{II}$	−0.120	0.0	
	−0.041	1.999	0.136
	0.093	0.636	0.317

[a] Values with respect to natural iron. [b] The line could not be resolved satisfactorily.

Chart I



Discussion

The stability of the mixed-valence species after allowance for statistical factors (K_c = 4) can be attributed to several factors,[2,39-43] the relative contributions of which we are interested in: (i) stabilization due to delocalization of the optical electron; (ii) stabilization due to structural changes as one goes from isovalent moieties to the mixed-valence moiety; (iii) stabilization due to purely Coulombic factors; (iv) variation in the magnetic interaction between the two paramagnetic centers via a "superexchange" pathway; (v) the inductive effect of a +3 charge discussed in ref 42.

$$\Delta G°_{tot} = \Delta G°_{del} + \Delta G°_{coul} + \Delta G°_{struct} + \Delta G°_{mag} + \Delta G°_{induc}$$

Among these factors, the contribution due to structural variations can be omitted in the case of ruthenium(II, III) and iron(II, III) mixed-valence compounds as the inner-sphere reorganizational effects are meager, when they form robust low-spin octahedral complexes. Similarly the contribution from the magnetic interaction can also be omitted as the bridging is through a triatomic species.[44]

The contribution due to the purely electrostatic factors has been evaluated in the past[2,41,42] for ruthenium (23) systems bridged by

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(34) Various interatomic distances of [FeNCSFe] and [FeNCSeFe] units were taken from the X-ray data reported in ref 32. The distances separating the metal centers were worked out to be 6.85 and 7.0 Å, respectively. The values are flexible by 10–20%.

(35) Work by D. N. Hendrickson on biferrocenium mixed-valence compounds should be mentioned in this regard.

(36) Ito, A.; Suenaga, M.; Ono, K. *J. Chem. Phys.* **1968**, *48*, 3597.

(37) Van Steenwijk, F. J.; Roder, P. *Helv. Phys. Acta* **1979**, *52*, 18.

(38) Mathur, H. B. In *Spectroscopy in Inorganic Chemistry*; Rao, C. N. R., Ferraro, J. R., Eds.; Academic: New York, 1970; Vol. I, p 347.

(39) Gagne, R. R.; Spiro, C. L.; Smith, T. J.; Hamann, C. A.; Thies, W. R.; Shiemke, A. K. *J. Am. Chem. Soc.* **1981**, *103*, 4073.

(40) Creutz, C. In ref 4, p 1.

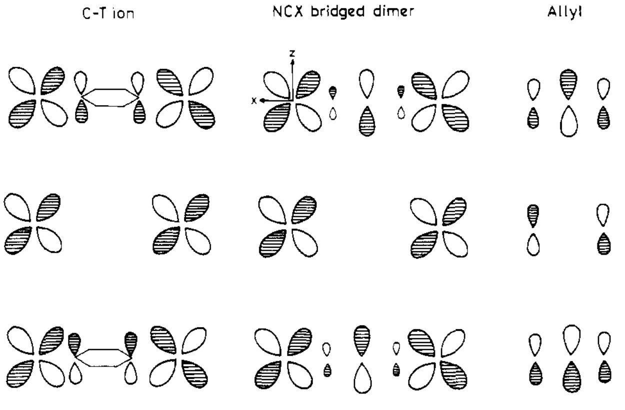
(41) Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.

(42) Sutton, J. E.; Sutton, P. M.; Taube, H. *Inorg. Chem.* **1979**, *18*, 1017.

(43) Pherlps, J.; Bard, A. J. J. *Electrochim. Acta* **1976**, *68*, 313.

(44) The "superexchange pathway" has been observed to be efficient in the case of monoatomic bridging ligands such as O^{2-}. This contribution could be neglected in the case of triatomic bridging as in our case.

Chart II. Interaction between the 3π LUMO Orbital of the NCX^- Ion in the *xz* Plane and the Filled dπ Orbitals of the Metal Centers[a]



[a] Allyl and C-T ion analogies are taken from ref 49. Similar overlap in the *xy* plane can be presumed.

neutral ligands on the basis of the point charge model in a dielectric continuum[45] and more recently on the basis of the more sophisticated ellipsoidal model.[46] Qualitatively,[2] the repulsive forces operative between the positive charges on the metal centers of a dimer can be given as

$$F \propto \frac{xy}{r^2}$$

where *x* and *y* are the magnitudes of charges and *r* is the distance of separation between charges. For the neutral-ligand-bridged dimeric compounds the repulsive forces operative on (22) (33) (state A; proportional to $2^2 + 3^2 = 13$) is 1 unit more than those operative on 2 (23) (state B; proportional to $2 \times 6 = 12$) and state B is stabilized over state A due to the greater repulsive forces, even when the electron delocalization is not "turned on". But the situation is completely different for dimers having anionic bridging ligands such as NCS^-, $NCSe^-$, and CN^- ions. Attractive forces are also operative apart from the repulsive forces in the case of anionic-ligand-bridged dimeric compounds. We can consider the dimer $[M_2L_b]$ (Chart I).

In a qualitative sense the resultant Coulombic contribution could be thought of as arising from the attraction between $(x+)$ and $(z-)$ of the M_1–L_b component and $(y+)$ and $(z-)$ of the M_2–L_b component and the repulsive forces between the $(x+)$ and $(y+)$ charges and this can be expressed as[47]

$$F_{\text{eff}} \propto \frac{xy}{r^2} - \left[\frac{xz}{r_1^2} + \frac{yz}{r_2^2}\right]$$

State B (proportional to 2) in this case is stabilized over state A (proportional to $0 + 3 = 3$) by the additional attractive forces. A value of 0.1–0.2 kcal mol^{-1} was obtained by Taube et al.[41,42] for $\Delta G°_{\text{coul}}$ for some of the weakly coupled ruthenium mixed-valence systems, and we expect this contribution should be, at the minimum, twice this amount in our case.

The contribution from electron delocalization, $\Delta G°_{\text{del}}$, is another crucial term in the NCX^--bridged compounds. A three-site model involving the back-bonding interaction of the dπ orbitals of both metal centers and the LUMO[29] (3π) orbitals of the chalcogenocyanate molecules can be presumed. The LUMO of the bridging molecules ($E_{3\pi(\text{SCN})} = -4.242$ eV)[48] could mix with dπ orbitals of metal centers of appropriate symmetry. Further, the 3π orbitals of chalcogenocyanate ions consist of more than 92% contribution[29] from the carbon 2p orbitals and a small amount of 2p orbitals of the end atoms, viz. N and S or Se, and are antibonding with respect to both the C–N and C–X (X = S, Se) bonds. A convenient treatment given by Ondrechen et al.[49] can be used. Among the split d orbitals of the metal centers in an octahedral environment, the combination $d_{xy}(1)$–$d_{xy}(2)$ and $d_{xz}(1)$–$d_{xz}(2)$ could interact with the degenerate 3π LUMO orbitals of the NCX^- ion to yield a pair each of antibonding, bonding, and nonbonding orbitals (Charts II and III).

Chart III. Qualitative MO Splitting Diagram for the NCX^--Bridged Pentacyanoferrate Dimers

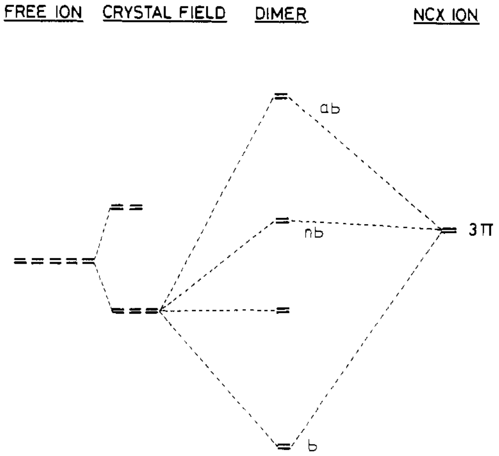
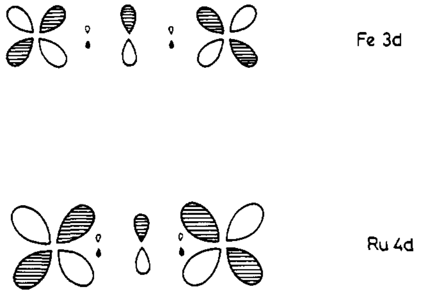


Chart IV. Effect of the Orbital Size on the $M(d\pi)$–$L_b(3\pi)$–$M(d\pi)$ Interaction



The charge distribution within the SCN^- ion has been calculated by di Sipio et al.[50] and Wagner[51] and is given as

S — C — N   di Sipio
-0.48 -0.01 -0.5
S — C — N   Wagner
-0.45 +0.19 -0.71

In both calculations the charge on the S atom remained the same but slightly different polarities for the C≡N group were observed. Further, from an ESCA investigation[52] of a few hexakis- and tetrakis(thiocyanato) complexes of transition metals, it has been observed that donation of electrons from the thiocyanato group results in a considerable reduction of charge on the S atom. The most interesting observation, however, is that there is a pronounced "back-donation" of electrons from the appropriate transition-metal ions to the carbon atom of the NCS^- ion. This back-donation must be the result of the interaction between the filled dπ orbitals of the transition-metal ions and the degenerate LUMO[53] orbitals

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(45) Kirkwood, J. G.; Westheimer, F. H. *J. Chem. Phys.* **1938**, *6*, 506, 513.
(46) Ehrenson, S. *J. Am. Chem. Soc.* **1976**, *98*, 7510.
(47) A positive sign for repulsive forces as they destabilize the system and a negative sign for attractive forces as they stabilize it have been used in a conventional sense.
(48) The energies of the 3π orbitals for NCO^- and NCS^- are given in ref 29, and the variation is not major. We have assumed that the $NCSe^-$ ion obeys the same trend, and as far as the energies of the 3π (LUMO) orbitals are concerned, the differences are small as we go from the NCO^- to the $NCSe^-$ ion.
(49) Ondrechen, M. J.; Ellis, D. E.; Ratner, M. A. *Chem. Phys. Lett.* **1984**, *109*, 50.
(50) Di Sipio, L.; Oleari, L.; de Michelis, G. *Coord. Chem. Rev.* **1966**, *1*, 7.
(51) Wagner, E. L. *J. Chem. Phys.* **1965**, *43*, 2728.
(52) Folkensson, B.; Larsson, R. *J. Electron. Spectrosc. Relat. Phenom.* **1982**, *26*, 157.

of SCN^- resulting in the growth of a considerable amount of negative charge on the carbon atom,[54] as is evident from the calculations of charge distributions from ESCA measurements.

Although the energy considerations[29,55,56] of the concerned molecular orbitals in the NCX-bridged dimers do not seem to allow an extensive mixing as in the case of the C-T ion,[49,57] there is a substantial mixing of the orbitals to stabilize the bridged species.

The solvent-dependent IT band (cf. Table VI) was found to be ~25% narrower than the calculated band (cf. Table VII). Bands narrower than the calculated ones have been observed earlier for strongly interacting systems.[15,58–60] Bands broader than the calculated ones were observed for weakly interacting systems.[42] The narrowness of the observed IT band suggests that the NCX^--bridged mixed-valence dimers could not be classified into the weakly interacting systems, though not in the strongly interacting category, e.g., pyrazine-,[58] cyanogen-,[59] and *tert*-butylmalononitrile-bridged[60] ruthenium dimers. Also the smaller amount of delocalization of the optical electron in the case of $[Fe(CN)_5NCXFe(CN)_5]^{6-}$ compared to that of $[Ru(NH_3)_5NCSRu(NH_3)_5]^{4+}$ [15] can be attributed to the larger mixing of the Ru 4d orbitals due to their larger size compared to that of Fe 3d orbitals (Chart IV).

The aforementioned arguments suggest that $\Delta G°_{del}$ should also be an important contributing factor to the total stability of the NCX^--bridging mixed-valence pentacyanoferrate dimers.

Further, it has been pointed out by Taube[61] on an earlier occasion[15] that the intrinsic asymmetry of the bridging ligand, viz., NCS^- ion, should increase the separation between the two redox stages further, apart from the contributions of the Franck–Condon barrier.[66] In this case, the enormous increase in K_c values and hence the stability of the mixed-valence species could not be explained in systems that are not comparatively strongly coupled as in our case.[62] This apparent paradox could be solved by studying systems, with strong coupling between metal centers through intrinsically asymmetric mediators. A probable candidate would be chalcogenocyanato-bridged osmium systems, where more mixing can be expected between the orbitals, favored by appropriate energy and spatial diffusion conditions.[63,64]

In conclusion, these studies on mixed-valence dimers bridged by asymmetric and anionic ligands indicate that the major factors contributing to the stability of the mixed-valence compounds over that of the isovalent ones are $\Delta G°_{coul}$ and $\Delta G°_{del}$. Other factors such as inherent instability of (22) species and the inductive effect of the 3+ charge in the mixed-valence state, discussed recently by Taube,[41] could also contribute.

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Registry No. $Na_5[Fe(CN)_5NCSFe(CN)_5]$, 110796-34-4; $Na_3[Fe(CN)_5(NH_3)]$, 14099-05-9; $(PPh_4)_5[Fe(CN)_5NCSFe(CN)_5]$, 110796-36-6; $Na_5[Fe(CN)_5NCSeFe(CN)_5]$, 110825-37-1; $(PPh_4)_5[Fe(CN)_5NCSeFe(CN)_5]$, 110796-38-8; $Rb_5[Fe(CN)_5SCNFe(CN)_5]$, 110796-39-9; $Rb_5[Fe(CN)_5SeCNFe(CN)_5]$, 110796-40-2; $Na_7[Fe(CN)_5SCNFe(CN)_5]$, 110796-41-3; $Na_7[Fe(CN)_5SeCNFe(CN)_5]$, 110796-42-4; $Rb_6[Fe(CN)_5SCNFe(CN)_5]$, 110796-43-5; $Rb_6[Fe(CN)_5SeCNFe(CN)_5]$, 110796-44-6; $[(C_2H_5)_4N]_6[Fe(CN)_5NCSFe(CN)_5]$, 110796-46-8; $[(C_2H_5)_4N]_5[Fe(CN)_5NCSeFe(CN)_5]$, 110796-47-9; $[(C_4H_9)_4N]_5[Fe(CN)_5NCSFe(CN)_5]$, 110796-48-0.

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(53) For the $[Pt(SCN)_4]^{2-}$ ion,[52] the negative charge on the carbon atom of the coordinated thiocyanato group is −0.35, which is far less than that of the free thiocyanate ion, viz., −0.01.

(54) According to di Sipio the degenerate LUMO orbitals are $\phi^{\pm}{}_{3\pi} = -0.307\chi_S\,(3p^{\pm}) + 0.729\chi_C\,(2p^{\pm}) - 0.612\chi_N\,(2p^{\pm})$, indicating that any electron donation to these orbitals will lead to the largest electron density on the carbon atom.

(55) Ondrechen, M. J.; Ratner, M. A.; Ellis, D. E. *J. Am. Chem. Soc.* **1981**, *103*, 1656.

(56) (a) Manoharan, P. T.; Gray, H. B. *J. Am. Chem. Soc.* **1965**, *87*, 3340. (b) Gray, H. B.; Beach, N. A. *Ibid.* **1963**, *85*, 2922.

(57) Fürholz, U.; Bürgi, H. B.; Wagner, F. E.; Stebler, A.; Ammeter, J. H.; Krausz, E.; Clark, R. J. H.; Stead, M. J.; Ludi, A. *J. Am. Chem. Soc.* **1984**, *106*, 121.

(58) Creutz, C.; Taube, H. *J. Am. Chem. Soc.* **1969**, *91*, 3988; **1973**, *95*, 1086.

(59) Tom, G.; Taube, H. *J. Am. Chem. Soc.* **1975**, *97*, 5310.

(60) Krentzien, H.; Taube, H. *J. Am. Chem. Soc.* **1976**, *98*, 6379.

(61) Taube, H., personal communication.

(62) The pyrazine- and cyanogen-bridged pentaammineruthenium mixed-valence dimers show very high comproportionation constants, viz., 10^6 and 10^{13}, respectively. The analogous dinitrogen-bridged osmium system shows a value of 10^{20}. When compared to these, the NCX^--bridged mixed-valence dimers could not be classified in the strongly interacting category.

(63) A brief perusal of the literature shows generally higher values of K_c and the ϵ_{max} of the IT band for osmium cases compared to ruthenium or iron cases, a result, probably, due to larger mixing of the molecular orbitals in the case of osmium.

(64) Palaniappan, V.; Agarwala, U. C., work in progress.

(65) The 3π LUMO orbitals of the bridging NCX^- ions have 92% contribution from the 2p orbital of the carbon atom. Hence, the situation could be thought of as a pseudosymmetric (Scheme II) rather than an asymmetric one as far as the $d\pi(Fe)-3\pi(NCX^-)-d\pi(Fe)$ skeleton is concerned, over which the optical electron is delocalized. Moreover, Hush treatment has been used earlier for asymmetrically bridged mixed-valence compounds (see ref 15 and 17).

(66) However, we assume that the π-framework over which the optical electron is delocalized could not be rigorously categorized into the asymmetric case. Also, the applicability of the pseudosymmetry[65] in the chemical sense is not clear and does not have any precedence. Appropriate comparisons with the mononuclear complexes could not be made as the S- or Se-bonded chalcogenocyanato complexes of the pentacyanoferrate moiety are not available. Synthesis of these S- and Se-bonded complexes and their electrochemical studies along with the already reported N-bonded complexes are under way.

(67) Sengupta, S. K.; Johri, U. C.; Singru, R. M.; Kunzru, D.; Srivastava, R. D. *J. Catal.*, in press.