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Electron Mediation through a Selenocyanate Bridge: Mono- and Dinuclear Ruthenium Diimine Complexes and Their Mixed-Valence Properties[1]

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Monomeric and selenocyanato-bridged dimeric complexes of bis(bipyridine)ruthenium(II/III) and their mixed-valence analogues were synthesized and characterized by various physicochemical techniques. The electronic (absorption and emission) and vibrational (IR and RR) spectral studies and the electrochemical properties are described. The mixed-valence compound $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]^{2+}$ exhibited Robin and Day class II behavior. The interaction between the metal centers is suggested to occur via a pseudosymmetrical π overlap, $d\pi(M)-3\pi^*(NCSe^-)-d\pi(M)$. The effects of nonbridging "spectator ligands" on the extent of metal-metal interaction are discussed.

Introduction

The interest in the chemistry of chalcogenocyanate ions arises from the interesting linkage isomerism it exhibits[2-6] and its ability to bridge between metal centers.[7] A number of chalcogenocyanato-bridged polymeric compounds were synthesized and studied. These polymeric compounds, if oxidized partially, might show interesting properties, as has been observed with low-dimensional materials such as ligand-bridged stacked-metal-complex systems.[8]

Recently,[9-11] we have reported the thiocyanato- and selenocyanato-bridged mixed-valence compounds of iron and ruthenium. The intervalence transfer (IT) bands observed in the near-IR region in conjunction with the Hush model[12] were used to evaluate the degree of metal-metal interaction in these compounds. The interaction via the chalcogenocyanate bridge in the binuclear complexes containing $[(NH_3)_5Ru]^{n+}$, $[(CN)_5Fe]^{n-}$, and $[(bpy)_2Ru]^{n+}$ units was suggested to occur via a pseudosymmetric[10] $d\pi(M)-3\pi^*(NCX^-)-d\pi(M)$ overlap. Further, it has been shown that the interaction is a function not only of the nature of the bridging units but also of the nonbridging "spectator ligands". It was also suggested that such interactions could possibly be "tuned" as to our needs by judiciously varying the nonbridging ligands.[11]

A few of the important results obtained from our earlier studies on the chalcogenocyanato-bridged mixed-valence compounds include the following:

(i) The thermodynamic barrier ΔE_0 for the optical and thermal electron transfer[13] arising from the intrinsic redox asymmetry of the bridging ligands is very small. Given that the $3\pi^*$-acceptor orbitals[14] of the chalcogenocyanate ions are mostly localized (>92%) on the central carbon atom and the contributions from the end atoms, viz., N and S or Se, are only meager, the pseudosymmetric nature[10] of the "π-bridge" is understandable.

(ii) The delocalization of the optical electron over the [M-NCX-M] unit is considerably affected by the nonbridging ligands.[11,15]

(iii) The π interactions in the selenocyanato complexes are slightly higher in energy than those in the corresponding thiocyanato ones. This difference in the π-bonding properties of thiocyanate and selenocyanate ligands could not be satisfactorily explained from the $3\pi^*$-acceptor orbital energy point of view, as the difference in energy is very small,[16] i.e., ~60 cm^{-1}.

(iv) The anionic nature of the bridging ligands could increase the stability of the mixed-valence species by favorably larger contributions[10] from the electrostatic factors, $\Delta G°_{\text{Coul}}$, to the total free energy change of the comproportionation reaction (1), $\Delta G°_{\text{tot}}$ (eq 2).

$$(22) + (33) \overset{K_{\text{com}}}{\rightleftharpoons} 2(23) \tag{1}$$

$$\Delta G°_{\text{tot}} = \Delta G°_{\text{coul}} + \Delta G°_{\text{del}} + \Delta G°_{\text{struct}} + \Delta G°_{\text{mag}} + \Delta G°_{\text{induc}} \tag{2}$$

A further confirmation of these results was obtained by a detailed study on the mixed-valence compounds of the selenocyanato-bridged bis(bipyridine)ruthenium(II/III) complexes. The outcome of such a study is presented in this paper.

Experimental Section

Materials. The complexes *cis*-$[(bpy)_2RuCl_2]\cdot 2H_2O$[17] and $[(bpy)_2Ru(NO)Cl](PF_6)_2$[17] were synthesized as described in the literature. Laboratory reagent grade ammonium hexafluorophosphate (Janssen Chimica), sodium tetraphenylborate (Sisco), sodium perchlorate (Riedel), potassium selenocyanate (Fluka AG), and AR grade potassium azide were used as procured. Solvents were dried by standard procedures and distilled before use. Doubly distilled water was used wherever mentioned. Cerium(IV) perchlorate solution was prepared[18] by dissolving Cerium(IV) hydroxide in 6 M perchloric acid and analyzed spectrophotometrically.

Preparations. (A) $[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$.[37] The compound was synthesized by a procedure[11] similar to that used for the synthesis of the analogous thiocyanate compound. However, unlike in the thiocyanate case, a 5-10-fold molar excess of potassium selenocyanate was sufficient. The product was washed well with water to remove the unreacted potassium selenocyanate. The purification was carried out on a Sephadex LH-20 column. A concentrated solution of $[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$

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(1) (a) (22), (23), and (33) represent the three different stages of oxidation states for the dimeric compound, and bpy represents 2,2'-bipyridine. (b) M-NCX and M-XCN represent the N- and X-bonded nature of the chalcogenocyanate ions (X = S, Se), and M-CNX is used to denote both the forms.

(2) (a) Parashad, R.; Yadav, S. K. S.; Agarwala, U. C. *J. Inorg. Nucl. Chem.* **1981**, *43*, 2359. (b) Parashad, R. Ph.D. Thesis, IIT, Kanpur, India, 1980. (c) Poddar, R. K.; Parashad, R.; Agarwala, U. C. *J. Inorg. Nucl. Chem.* **1980**, *42*, 837.

(3) (a) Yadav, S. K. S.; Agarwala, U. C. *Polyhedron*, **1984**, *3*, 1. (b) Yadav, S. K. S. Ph.D. Thesis, IIT, Kanpur, India, 1982. (c) Yadav, S. K. S.; Agarwala, U. C. *Indian J. Chem., Sect. A* **1982**, *21A*, 175.

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

(5) (a) Jackson, W. G.; Hookey, C. N. *Inorg. Chem.* **1984**, *23*, 668. (b) Jackson, W. G.; Jurrisson, S. S.; McGregor, B. C. *Inorg. Chem.* **1985**, *24*, 1788.

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

(7) (a) Manoli, J. M.; Potvin, C.; Secheresse, F.; Marzak, S. *J. Chem. Soc., Chem. Commun.* **1986**, 1557. (b) Taniguchi, M.; Sugita, Y.; Ouchi, A. *Bull. Chem. Soc. Jpn.* **1987**, *60*, 1321. (c) Nakao, Y.; Nakamura, H.; Mori, W.; Sakurai, T.; Suzuki, S.; Nakahara, A. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2755.

(8) (a) Miller, J. S.; Epstein, A. J. *Prog. Inorg. Chem.* **1976**, *20*, 1. (b) *Ann. N.Y. Acad. Sci.* **1978**, *313*.

(9) Palaniappan, V.; Yadav, S. K. S.; Agarwala, U. C. *Polyhedron* **1985**, *4*, 1457.

(10) Palaniappan, V.; Singru, R. M.; Agarwala, U. C. *Inorg. Chem.* **1988**, *27*, 181.

(11) Palaniappan, V.; Sathaiah, S.; Bist, H. D.; Agarwala, U. C. *J. Am. Chem. Soc.*, in press.

(12) (a) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (b) Hush, N. S. *Electrochim. Acta* **1968**, *13*, 1005.

(13) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(14) di Sipio, L.; Oleari, L.; de Michelis, G. *Coord. Chem. Rev.* **1966**, *1*, 7.

(15) Henderson, W. W.; Shepherd, R. E. *Inorg. Chem.* **1985**, *24*, 2398.

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

(17) Goodwin, J. B.; Meyer, T. J. *Inorg. Chem.* **1971**, *10*, 471.

(18) Vogel, A. I. *A Textbook of Quantitative Inorganic Chemistry*, 2nd ed.; Longmans: London, 1951.

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crude product in acetonitrile was sorbed onto the column top (50 × 2 cm). The major amount of the compound was eluted in a single band by using a 1:3 acetonitrile:methylene chloride mixture. This was separated from the concentrated eluate by adding an excess of diethyl ether. Yield: 70–80%.

Anal. Calcd for $C_{22}H_{20}N_6O_2RuSe_2$: C, 40.06; H, 3.03; N, 12.75. Found: C, 40.38; H, 3.81; N, 12.65.

(B) $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$. This compound was prepared by two different procedures described elsewhere[11] for the analogous thiocyanato complex. (a) A saturated methanolic solution of potassium selenocyanate was added to the solvenato complex $[(bpy)_2Ru(acetone)Cl]^+$ generated in situ from $[(bpy)_2Ru(NO)Cl](PF_6)_2$ (202.3 mg) and an equimolar amount of potassium azide (21.4 mg) in acetone (20–25 mL). The resulting solution after being stirred for 1 h was filtered into an excess of stirred diethyl ether. The precipitated crude product was filtered and washed extensively with water (four 10-mL portions to remove the unreacted potassium selenocyanate) and finally with ether. Recrystallization from acetone/diethyl ether yielded a brownish red product. It was further purified by gel filtration as described in part A. Elution with a 1:3 acetonitrile/methylene chloride mixture resolved the crude product into two bands on the column. On the basis of retention times, the compound from the major second band was identified as the desired monomeric product, which was separated by precipitation from the eluate with an excess of diethyl ether. Yield: 60–70%. (b) The red-brown $[(bpy)_2Ru(H_2O)Cl]^+$ solution was generated by refluxing the complex *cis*-$[(bpy)_2RuCl_2]\cdot 2H_2O$ (100 mg) in water (15–20 mL). The solution was filtered through a fine-porosity glass frit, and the filtrate was cooled to room temperature. An aqueous solution (5–10 mL) of 5-fold molar excess of potassium selenocyanate was added to this with stirring. The dark compound, which precipitated immediately, was filtered and washed extensively with water to remove the unreacted potassium selenocyanate and finally rinsed with ether. This was recrystallized and purified as described in part B(a). The yield was slightly better than that obtained by procedure B(a).

In both the procedures B(a) and B(b), the gel filtration step enabled us to separate another compound in small amounts. On the basis of the position and integrated intensity[19] of the ν(CN) band in the vibrational spectrum, it was identified to be the linkage isomer, viz., $[(bpy)_2Ru(SeCN)Cl]\cdot xH_2O$.

Anal. Calcd for $C_{21}ClH_{20}N_9O_2RuSe$: C, 42.71; H, 3.39; N, 11.86. Found: C, 42.86; H, 3.26; N, 12.11.

(C) $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]Y$ ($Y^- = BPh_4^-, ClO_4^-, PF_6^-$). The ethanol (15–20 mL) solution of $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$ (100 mg) was added to an equimolar aqueous solution of $[(bpy)_2Ru(H_2O)Cl]^+$, generated from an appropriate amount of *cis*-$[(bpy)_2RuCl_2]\cdot 2H_2O$ as described in part B(b). The resulting mixture was degassed by bubbling dinitrogen (10–15 min), and the solution was refluxed for 2 h, with a continuous stream of dinitrogen over the mixture. The solution was filtered into a saturated aqueous solution of sodium perchlorate, sodium tetraphenylborate, or ammonium hexafluorophosphate. The flocculent brownish red precipitate was filtered, washed with ether, and dried. Yield: 95%. Chromatographic purification of the binuclear complex was carried out by using an alumina column (50 × 3 cm). A concentrated solution of the crude product was charged onto the column top. The elution was carried out using a 1:9 acetonitrile:benzene or acetonitrile:methylene chloride mixture and slowly enriching the content of acetonitrile in the mixture to an approximately 2:3 proportion. The major band that moved on the column was eluted, and the compound was precipitated from the eluate with diethyl ether. Yield: 80–85%. Small amounts of the monomeric impurities were discarded.

Anal. Calcd for $BC_{65}Cl_2H_{52}N_9Ru_2Se$: C, 59.05; H, 3.94; N, 9.54. Found: C, 59.64; H, 4.33; N, 9.02.

(D) $[(bpy)_2Ru(NCSe)X]Y$ ($X^- = Cl^-, SeCN^-$; $Y^- = PF_6^-, BPh_4^-$). The oxidation of the ruthenium(II) monomeric compounds was carried out by using cerium(IV) perchlorate solution. A stoichiometrically equimolar solution of Ce(IV) was added with stirring to a solution of $[(bpy)_2Ru(NCSe)X]$ ($X = Cl^-, SeCN^-$) in acetone, kept in reduced light. The stirring was continued for 0.5 h. Excess of the anion (sodium tetraphenylborate or ammonium hexafluorophosphate) was added to this solution, which was then filtered into an excess of stirred diethyl ether. The complexes $[(bpy)_2Ru(NCSe)Cl]Y$ (dark purple) or $[(bpy)_2Ru(NCSe)_2]Y$ (red orange) ($Y^- = BPh_4^-, PF_6^-$) were filtered and washed with water and ether. These were recrystallized with acetone/diethyl ether. The purity of the compounds was checked by passing them through a Sephadex LH-20 column, where they showed a single band.

Anal. Calcd for $BC_{46}H_{36}N_6RuSe_2$: C, 58.60; H, 3.82; N, 8.92. Found: C, 58.22; H, 4.03; N, 8.66. Calcd for $BC_{45}ClH_{36}N_5RuSe$: C, 61.86; H, 4.12; N, 8.02. Found: C, 61.50; H, 3.84; N, 7.95.

(E) $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl](BPh_4)_3$. This was prepared by a procedure similar to that described in part D except that a little excess over the stoichiometric 2 equiv of Ce(IV) was used for oxidizing the complex. The red-orange compound thus obtained in quantitative yield was washed with water and ether.

Anal. Calcd for $B_3C_{113}Cl_2H_{92}N_9Ru_2Se$: C, 69.22; H, 4.70; N, 6.43. Found: C, 69.70; H, 5.05; N, 6.95.

(F) $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl](BPh_4)_2$. The mixed-valence compound was prepared by mixing the stoichiometrically equimolar solutions of the complexes (22) and (33) in acetonitrile. The tetraphenylborate salt that separated out from this solution showed a near-IR band with slightly reduced intensity similar to that of the (23) compound generated in situ by the oxidation of (22) using $[Fe(bpy)_3]^{3+}$ in acetonitrile.

The hydration in some of the compounds was verified by recording their ^1H NMR spectra in DMSO-d_6 solvent. The signal due to the lattice water molecules appeared around 4.7 ppm. The convenience of using tetraphenylborate as the anion has been mentioned elsewhere.[11]

Physicochemical Methods. The details of the physicochemical methods are described elsewhere.[4,10,11] The emission spectra were recorded, at the first instance, on an indigenously assembled scanning spectrofluorometer described earlier.[20] The excitation using a 150-W Xe–Hg lamp at different wavelengths that overlap the MLCTs of the compounds and detection using an IP 28 photomultiplier tube did not yield any emission. Hence, the sensitivity of the instrument was taken as the upper limit of ϕ_{em} for the emission present, if any. However, with excitation using Ar ion laser lines (Spectraphysics 165-09) and detection using a cooled PMT (C 31034) of the Spex spectrophotometer described earlier,[21] the emission maxima were detected. Here again, the quantum yields of the emission could not be evaluated accurately, as the samples underwent local burning due to a high-power exciting laser. Hence, the ϕ_{em} was taken to be proportional to the intensity of the observed emission profiles of the monomeric and dimeric compounds, assuming a constant local burning in both cases. The spectra were recorded after equal time intervals from the mounting of the samples.

The details of CV measurements have been described earlier.[10] Millimolar solutions of the compounds in dichloromethane or acetonitrile were employed. Tetrabutylammonium perchlorate was used as the supporting electrolyte. Potentials are referenced to the SCE. Raman spectra were obtained as described elsewhere.[11] Near-IR spectra were obtained by using a Hitachi MU-3400 spectrophotometer. The sample solutions were taken in 1-cm matched quartz cells. The extinction coefficient values were calculated by recording the absorptions at least in two different concentrations.

Results

Infrared Spectra. The infrared spectra of all the compounds exhibited bands characteristic of the coordinated 2,2′-bipyridine moiety. Mononuclear complexes, viz., $[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$ and $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$, showed peaks due to lattice water molecules around 1640 and 3450 cm^{-1}. The presence of the lattice water molecules was further corroborated by the microanalytical and ^1H NMR spectral studies. The integrated intensity of the δ 4.7 signal corresponded to two molecules of water. The bands due to the ν(CN) of the selenocyanate ligand were observed around 2083 and 2123 cm^{-1} for $[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$ and $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$, respectively. The integrated intensities of these bands in acetonitrile solution were obtained by using Ramsay's method.[6] The position and the integrated intensity (A) of the ν(CN) band, viz., 8×10^4 and 9.1×10^4 $M^{-1}\ cm^{-2}$, respectively, suggest the N-bonded nature of the selenocyanate group. Similar values for integrated intensities of ν(CN) bands have been obtained earlier for $[(bpy)_2Ru(NCS)_2]$[22] (10.1×10^4 $M^{-1}\ cm^{-2}$) and $[(bpy)_2Ru(NCS)Cl]\cdot 2H_2O$[11] ($12 \times 10^4$ $M^{-1}\ cm^{-2}$), where the thiocyanate groups are coordinated through the nitrogen end. Further, the ν(CN) band for $[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$ around 2083 cm^{-1} is split, showing a clear shoulder at 2120 cm^{-1}. Such splitting has been observed

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(19) The integrated intensity of the ν(CN) band for the Se-bonded isomer as obtained from acetonitrile solution is 3×10^4 $M^{-1}\ cm^{-2}$, while the value for the dimeric compound was considerably higher, viz., 40×10^4 $M^{-1}\ cm^{-2}$. The values for the free, N-bonded, and S- or Se-bonded chalcogenocyanates are respectively $(3–5) \times 10^4$, 9×10^4, and 2×10^4 $M^{-1}\ cm^{-2}$.[6]

(20) Swaminathan, M.; Dogra, S. K. *Indian J. Chem., Sect. A* **1983**, *22A*, 853.

(21) Lamba, O. P.; Bist, H. D.; Jain, Y. S. *Can. J. Chem.* **1983**, *61*, 608.

(22) Wajda, S.; Rachlewicz, K. *Inorg. Chim. Acta* **1978**, *31*, 35.

Table I. Infrared Spectral Data (cm^{-1})[a]

complex	bands
$[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$	2120 (sh), 2083 (s), 660, 485, 430, 360, 290, 3380–3500,[b] 1650[b]
$[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$	2123 (vs), 630 (w), 445 (w), 430, 375, 355, 335, 300, 290, 3450,[b] 1640[b]
$[\{Cl(bpy)_2Ru\}_2NCSe]BPh_4$	2130 (s), 627 (m), 510, 485, 430, 370, 345, 320, 290
$[\{Cl(bpy)_2Ru\}_2NCSe](BPh_4)_3$	2095 (s)
$[\{Cl(bpy)_2Ru\}_2NCSe](BPh_4)_2$	2085 (s)

[a] Spectra were recorded for KBr/CsI pellets; characteristic peaks due to anions and coordinated 2,2′-bipyridine are not given here. [b] Water of crystallization.

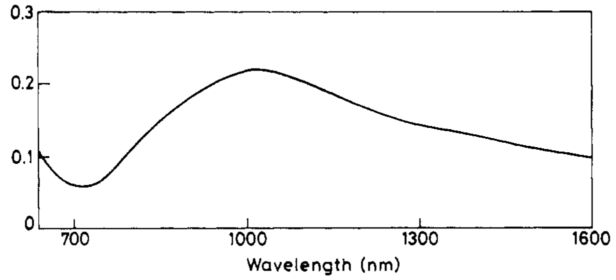
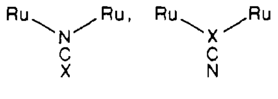


Figure 1. Near-IR spectrum of $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]^{2+}$ in acetonitrile. The concentration used is $\sim 5 \times 10^{-4}$ M.

earlier[6,23] for *cis*-dithiocyanato complexes, such as *cis*-$[(NH_3)_4Ru(CNS)_2]$.[1] Coupling between the vibrational modes of the two chalcogenocyanato groups at cis positions could lead to a splitting of the ν(CN) signal.

The position of the ν(CN) band for the binuclear complex (22) is only slightly shifted (2130 cm^{-1}) from that of the monomeric $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$. However, the position of the ν(CN) band does give a conclusive clue as to the structure of the [Ru–NCSe–Ru] bridge. Amoung the three possibilities[6] of the chalcogenocyanato bridging, viz.



and Ru–NCX–Ru, the last possibility is the most probable one. The first possibility could be ruled out because it should give a considerably low value for the ν(CN) mode, as there will be extensive π back-donation from both the ruthenium metal centers. The second possibility, as such, is not favorable[11,22,24] as the "spectator ligands" are strongly π-acidic, and under such circumstances the formation of X-bonded compounds is highly unfavorable. Thus, the position of the ν(CN) band around 2130 cm^{-1} conforms well with the linear-bridged structure.[6] All the other characteristic bands due to ν(CSe) and δ(NCSe) modes were observed at their respective positions and are given in Table I.

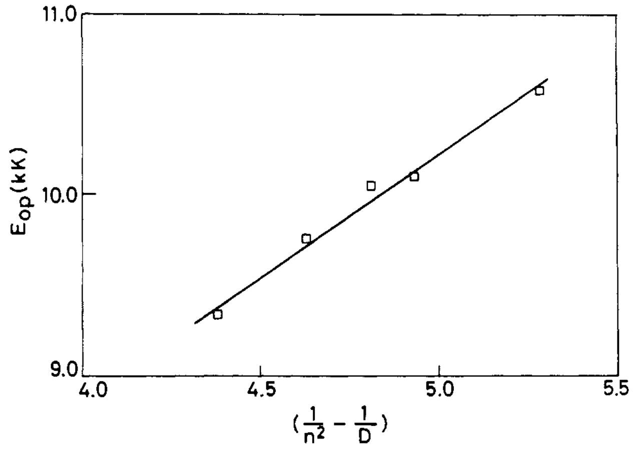


Figure 2. Plot of $1/n^2 - 1/D$ vs E_{op} for the IT transition of the $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]^{2+}$ ion.

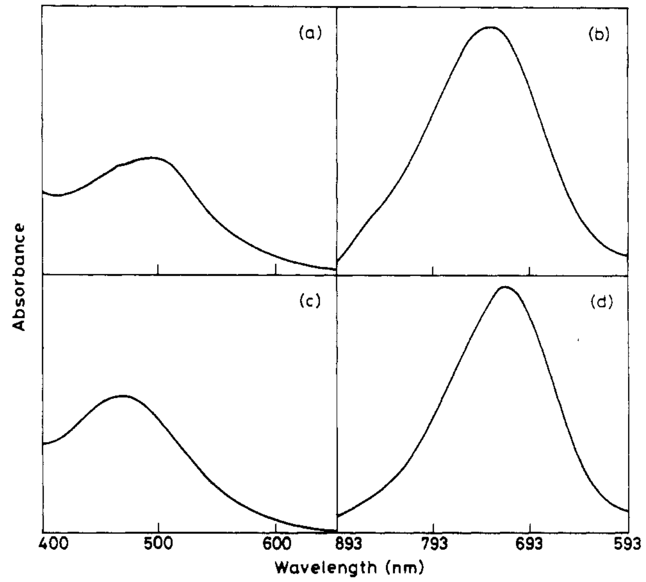


Figure 3. Absorption (a) and emission (b) spectra of $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$ and absorption (c) and emission (d) spectra of $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]BPh_4$ in acetonitrile. λ_{ex} for emission spectra is 514.5 nm.

Emission and Absorption Spectra. The electronic absorption spectral data are presented in Table II. Apart from the intraligand (π–π^*) transitions[25] observed around 240 and 290 nm, all the compounds showed an intense band in the 215-nm region. This could involve contributions from the intraligand transition of the coordinated selenocyanate group.[6] Further, the lowest energy charge-transfer band, among the MLCTs observed in the visible and UV regions, is generally broader and exhibits intense shoulders that appear at higher energies in monomeric compounds and at lower energies in dimeric compounds. They are attributed to a $d\pi(Ru)$–$3\pi^*(NCSe^-)$ MLCT transition. A similar observation was made with the analogous thiocyanato compounds[11] recently. The assignments are further justified by the resonance Raman studies (vide supra). The completely oxidized (33) compound exhibited a largely blue-shifted band with somewhat higher intensity.[25]

The intervalance transfer (IT) band for the (23) complex in acetonitrile was located around 945 nm (Figure 1). The fwhm, $\Delta\bar{\nu}_{1/2_{obsd}}$, of this weak band ($\epsilon_{IT}$ = 450 cm^{-1} M^{-1}) was in good agreement with the fwhm, $\Delta\bar{\nu}_{1/2_{calcd}}$, calculated by using the Hush model.[12] Further, the solvatochromism (Table III) associated with the IT band was in concordance with the dielectric continuum model.[12] A linear correlation between $1/n^2 - 1/D$, where n^2 and D are the optical and static dielectric constants of the solvent, and E_{op} was obtained (Figure 2), suggesting that the mixed-valence (23) ion falls in the class II category of the Robin and Day[26] classification scheme. Various parameters such as oscillator strength (f) of the IT band, dipole strength (D), transition dipole moment ($|M|$), interaction parameter (H_{AB}), and the delocalization factor (α^2) were calculated by using the near-IR band parameters and the Hush equations.[12,13] These are listed in Table IV. The values of the interaction parameter, H_{AB}, and the delocalization factor, α^2, viz., 465 cm^{-1} and 1.9×10^{-3} in acetonitrile, can be

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(23) Palaniappan, V.; Agarwala, U. C., unpublished results.

(24) (a) Gutterman, D. F.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 1727. (b) Huheey, J. E. *Inorganic Chemistry—Principles of Structure and Reactivity*, 2nd ed. (International SI Edition); Harper: Cambridge, England, 1983; pp 516–521.

(25) (a) Bryant, G. M.; Fergusson, J. E.; Powell, H. K. J. *Aust. J. Chem.* **1971**, *24*, 257. (b) Bryant, G. M.; Fergusson, J. E. *Aust. J. Chem.* **1971**, *24*, 275. (c) Johnson, E. C.; Callahan, R. W.; Eckberg, R. P.; Hatfield, W. E.; Meyer, T. J. *Inorg. Chem.* **1979**, *18*, 618.

(26) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

Table II. Electronic Spectral Data for the Monomeric and Dimeric Bis(bipyridine)ruthenium(II/III) Complexes[a]

$[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$		$[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$	$[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]^{n+\,b,c}$		
Ru(II)	Ru(III)[b]	Ru(II)	(22)	(23)	(33)
				945 (450)	
			540 (sh) (~3000)	550 (sh)	
493 (6350)		478 (5110)	469 (9000)	459 (15 760)	456 (16 200)
440 (sh) (3850)	421 (7540)	430 (sh) (~4000)			
	385 (sh) (5000)				
343 (5720)	315 (sh)	339 (5830)	342 (10 520)	337 (18 000)	334 (18 000)
292 (27 740)	285 (46 350)	286 (15 800)	288 (44 235)		287 (91 000)
245 (21 665)		244 (15 230)	237 (44 120)		232 (93 200)
214 (30 380)	220 (53 350)	225 (14 960)	220 (46 000)		222 (103 900)

[a] Wavelengths are in nm; extinction coefficients in M^{-1} cm^{-1} are given in parentheses; spectral data of samples in acetonitrile solutions. [b] Tetraphenylborate salts of the oxidized species. [c] Data in the UV region for (23) were not obtained.

Table III. Solvent-Dependent Near-IR Spectral Data for $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]^{2+}$[a]

solvent	$1/n^2 - 1/D$[b]	$\bar{\nu}_{IT}$, cm^{-1}	ϵ_{IT}, M^{-1} cm^{-1}
acetonitrile	0.528	10 582	450
acetone	0.493	10 101	493
propylene carbonate	0.481	10 050	
N,*N*-dimethylformamide	0.463	9 756	
dimethyl sulfoxide	0.438	9 346	

[a] Tetraphenylborate salt; the spectrum obtained for the solid in acetonitrile was identical with that for species generated in situ by $[Fe(bpy)_3]^{3+}$ oxidation in acetonitrile, except for a slight decrease in the extinction coefficient. [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.

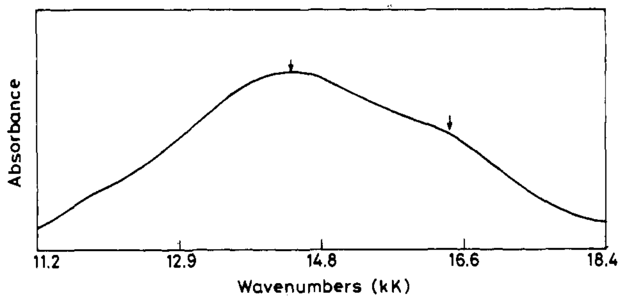

Figure 4. Emission spectrum of the dimer $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]BPh_4$ in acetonitrile (λ_{max} = 469 nm). λ_{ex} for emission spectra is 476 nm.

compared with those for the analogous thiocyanate compound, viz., 453 cm^{-1} and 1.85 × 10^{-3}.

The fluorescence spectra for the monmeric $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$ and dimeric $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl](BPh_4)$ in the solid state and in acetonitrile solution were obtained at room temperature (Figure 3). The relevant data are given in Table V. In general, the selenocyanate compounds fluoresce 10-fold less than their thiocyanate analogues.[11] The dimer emission is quenched (10-fold) considerably. The emission maximum of the dimeric compound is red-shifted by ~1000 cm^{-1} from that of the monomer emission, suggesting interaction between the metal centers via a chalcogenocyanate bridge. Further, the excitation spectra of the emission in both monomeric and dimeric compounds (cf. Table V) suggest the emissive state populated within the excitation wavelength interval employed, viz., 457.9–514.5 nm, is the same. The solvatochromism associated with the dimer emission was considerably larger than that with the monomer (cf. Table V). The excitation of the dimeric compound (λ_{max} = 469 nm) at 476.5 nm yielded an emission spectrum, which exhibited a clear shoulder (Figure 4). The separation of the shoulder from the prominent band maximum, viz., ~1500 cm^{-1}, suggests that this might be a vibrational structure. The vibrational modes of the bipyridine rings observed around 1480 and 1550 cm^{-1} seem to be strongly coupled with the MLCT excited state of this band. Thus, it was concluded that the emissive level is localized on the bipyridine coligands.

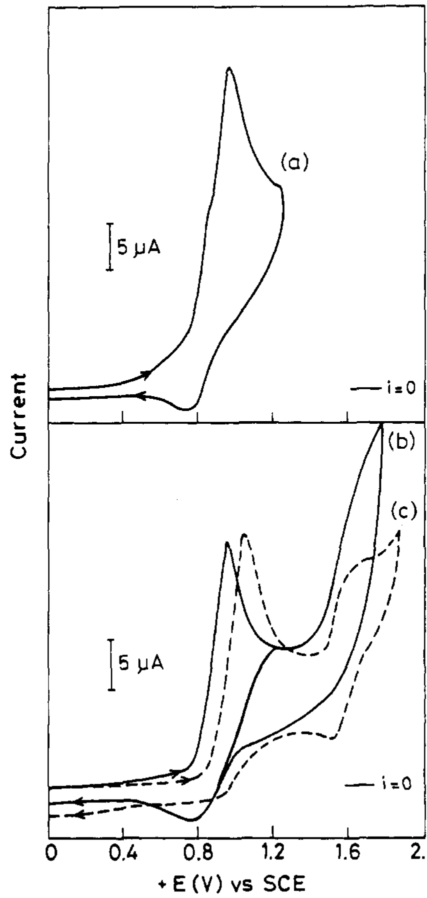

Figure 5. Cyclic voltammograms (oxidative scan) of the selenocyanate dimer $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]BPh_4$ in methylene chloride (a) and acetonitrile (b) (scan rate = 100 mV s^{-1} in both cases) and of the analogous thiocyanate dimer (c) (scan rate = 200 mV s^{-1}). The supporting electrolyte is 0.1 M TBAP. The shoulder is clearly visible in (a).

Resonance Raman Spectra. Resonance Raman spectra for the monomeric and dimeric compounds $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$ and $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl](BPh_4)$ were recorded by using

Table IV. Characteristic Parameters Calculated from IT Bands and Hush Formulas for $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]^{2+}$[a,b]

solvent	$\bar{\nu}_{IT}$, cm^{-1}	ϵ_{IT}, M^{-1} cm^{-1}	$\Delta\bar{\nu}_{1/2_{obsd}}$, cm^{-1}	$\Delta\bar{\nu}_{1/2_{calcd}}$, cm^{-1}	$10^2 f$[c]	*D*,[c] Å	$10^{10}\vert M\vert$,[c] Å esu	λ_1,[c] cm^{-1}	λ_0,[c] cm^{-1}	H_{AB},[c] cm^{-1}	$10^3\alpha^2$[c]
acetonitrile	10 582	450	5445	4994	1.13	0.314	1.51	3753	7112	465	1.90
acetone	10 101	493	4463	4830	1.01	0.304	1.46	3753	6640	425	1.76

[a] Tetraphenylborate salt. [b] For various parameters, see the text. [c] Calculated by using the "Hush formulas".

Table V. Emission Spectral Data[a]

	$[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$		$[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]BPh_4$	
λ_{ex}, nm	λ_{em}, cm^{-1}	$\Delta\bar{\nu}_{1/2}$, cm^{-1} [b]	λ_{em}, cm^{-1}	$\Delta\bar{\nu}_{1/2}$, cm^{-1} [b]
457.9	14 240	2360	13 560	2440
476.5	14 280[c]	2500[c]	14 775[c]	3220[c]
			~16 300 (sh)	
514.5	14 425	2220	13 380	2500
			14 100[c]	2500[c]

[a] Spectra were recorded for solid samples; error ±50 cm^{-1}. [b] Fwhm. [c] Spectra recorded in acetonitrile solution.

Table VI. Resonance Raman Spectral Data (cm^{-1})[a]

$[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$		$[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]BPh_4$	
λ_{ex} = 476.5 nm	λ_{ex} = 457.9 nm	λ_{ex} = 476.5 nm	λ_{ex} = 514.5 nm
302			326
374 (10)	373 (3.0)	373 (3.3)	376 (1.7)
494 (6)[b]	489 (2.5)[b]	489 (4.0)[b]	468 (1.0)[b]
			496 (1.0)
1022 (15)	1021 (4.1)	1021 (4.3)	1020 (sh) (1.7)
			1036 (2.2)
1166 (20)	1166 (6.0)	1161 (7.0)	1160 (4.0)
1266 (13)	1265 (5.0)	1261 (4.3)	1264 (1.6)
1310 (38)	1309 (10)	1305 (11)	1307 (3.2)
1478 (78)	1480 (21)	1477 (26)	1480 (9.9)
1550 (55)	1550 (17)	1553 (17)	1556 (5.6)
1594 (53)	1593 (15)	1597 (15)	1600 (5.0)
	*2120 (2.0)		*2128 (w) (1.0)
2249 (10)	2250 (10)	2251 (10)	2250 (10)

[a] Spectra were recorded for acetonitrile solutions in 1-mm-i.d. capillary tubes; the relative intensity values parentheses were calculated by using the ν(CN) of CH_3CN as the reference; the peaks denoted by asterisks are due to coordinated selenocyanate ions. [b] Broad.

the excitations with Ar ion laser lines in the interval of 457.9–514.5 nm. These lines overlap with the lowest energy MLCT bands of the compounds to different degrees. All excitations showed the characteristic seven-line pattern[27] of the coordinated 2,2′-bipyridine, but with markedly different intensities (cf. Table VI). Besides, the monomeric compound when excited with the 457.9-nm line showed a weak band at 2120 cm^{-1} attributable to the ν(CN) mode of the selenocyanate group. Similarly, excitation using the 514.5-nm line yielded the ν(CN) band around 2128 cm^{-1} for the dimeric compound. This suggests that the MLCT corresponding to the Ru–NCSe group lies toward the higher energy in the case of the monomer, while it is considerably red shifted in the dimer. This in turn suggests that the $3\pi^*(NCSe^-)$-acceptor orbitals are stabilized in the dimer by the interaction with the $d\pi$ orbitals of ruthenium. Lack of facilities to excite the MLCT bands at further higher and lower energies did not allow us to clarify this point more clearly.

Electrochemistry. The essential data of the electrochemical studies of the compounds as obtained from cyclic voltammetric measurements are given in Table VII. Representative voltammograms are illustrated in Figure 5. The monomeric complexes $[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$ and $[(bpy)_2RuNCSeCl]\cdot 2H_2O$ exhibited Ru(II/III) couples at 0.32 and 0.59 V, respectively. Apart from this, these compounds exhibited another wave at slightly more positive potentials, viz., 0.9–1.0 V (cf. Table VII). This peak seems to be slightly complicated, as the separation between the peak potentials of this wave is large. Chemical oxidations to separate this product are under way.[28] The peak potentials for these redox processes are scan rate dependent, and a plot of $v^{1/2}$ vs ΔE_p, where v is the scan rate and $\Delta E_p = E_{pa} - E_{pc}$, is linear with intercept values in the range 60–80 mV, larger than the theoretical value, 59 mV.[29] Further, the ratio of the peak currents for anodic and cathodic parts of these waves, i_{pc}/i_{pa}, is close to unity (≈0.9), suggesting the reversible one-electron nature of these redox processes.[29]

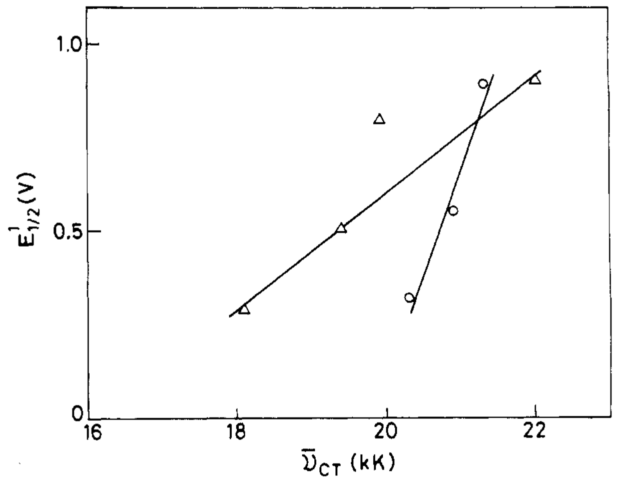

Figure 6. Plot of $\bar{\nu}_{CT}$ vs $E_{1/2}^{(1)}$ for the thiocyanato (Δ) and selenocyanato (O) compounds.

The electrochemistry of the dimer is interesting. It shows two waves corresponding to the successive (22)–(23) and (23)–(33) oxidations, which are poorly separated. The separation between the anodic wave corresponding to (23)–(33) oxidation and the cathodic wave corresponding to (23)–(22) reduction varied between 160 and 290 mV in the range of scan rates employed, viz., 50–400 mV s^{-1}. The variation was linear with respect to $v^{1/2}$, where v is the scan rate. The addition of two successive one-electron reversible steps, which are poorly resolved, could show such a behavior. The variation of the peak current, i_p, with respect to the scan rate, v, was examined. A plot of ln v vs ln i_p was linear with slope values suggesting a diffusion-controlled process. The current function, $i_{pc}/v^{1/2}$, was also invariant, as is observed for reversible processes. A similar observation has been made earlier[11] for the corresponding thiocyanate compound. However, due to the poor resolution of the two waves, an accurate value for the comproportionation constant, K_{com}, could not be obtained, and only an upper limit of $K_{com} < 350$ could be predicted. Further, the dimer showed another two-electron wave at a more positive potential ($E_{pa} \approx +1.6$ V). This peak is irreversible, as evident from the absence of the cathodic part of this wave. However, the analogous thiocyanate compound exhibited a more defined wave ($E_{1/2} = +1.55$ V), corresponding to a two-electron change (Figure 5). Chemical oxidation of the (22) species using 4 equiv of Ce(IV) yielded a compound that probably has thiocyanato-bridged Ru(IV) moieties. However, a more careful study is necessary to clarify this point.[28]

Discussion

The $d\pi-\pi_1$(bpy) MLCT energies show a linear correlation with the first oxidation potentials of the compounds $[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$, $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$, and the dimeric $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]BPh_4$. A similar correlation is also obtained for the corresponding thiocyanato compounds. However, the slope of the linear plot $\bar{\nu}_{CT}$ vs $E_{1/2}^{(1)}$ (Figure 6) for the selenocyanate compounds is approximately 4-fold greater than that for the thiocyanate compounds. This suggests that the "π disturbances" in the selenocyanate compounds are greater than that in the thiocyanate compounds. Earlier studies[4,6] on the chalcogenocyanate complexes of pentaammineruthenium(III) suggest that the π back-bonding in the $[M-CNSe]^+$ unit is stronger than that in the $[M-CNS]^+$ unit. Selenocyanate ion, being a better π acid, could compete more than thiocyanate ion with the 2,2′-bipyridine "spectator ligand", which is a good π

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(27) Smothers, W. K.; Wrighton, M. S. *J. Am. Chem. Soc.* **1983**, *105*, 1067.
(28) Work in progress.
(29) (a) Nicholson, R. S.; Shain, I. *Anal. Chem.* **1964**, *36*, 706. (b) Bard, A. J.; Faulkner, L. R. *Electrochemical Methods—Fundamentals and Application*, 1st ed.; Wiley: New York, 1980.

Table VII. Electrochemical Data for the Bis(bipyridine)ruthenium(II/III) Complexes in Methylene Chloride[a]

	oxidn			redn		
complex	$E_{1/2}^{(1)}$	$E_{1/2}^{(2)}$	$E_{1/2}^{(3)}$	$E_{1/2}^{(4)}$	$E_{1/2}^{(5)}$	$E_{1/2}^{(6)}$
$[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$	+0.32 (60)	+0.98 (115)		-1.36^b		
$[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$	+0.59 (74)	+0.92 (111)		-1.52 (166)^b		-1.97 (74)
$[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]BPh_4$	+0.89 (85)^b		$+1.55^d$	-1.26 (80)	-1.50 (80)	
	+0.87 (116)^{b,c}			-1.36 (100)^{b,c}		

[a] The potential values in volts are referred to the SCE at room temperature; error is ±0.02 V; ΔE_p values given in the parentheses were obtained from the intercept values of the $v^{1/2}$ vs E_p plots by extrapolation (see text). [b] Overlapping waves. [c] In acetonitrile. [d] Poorly defined irreversible wave.

acceptor by itself, for π back-donation from the metal centers. This in turn could lead to a slight destabilization of the π-acceptor orbitals of the 2,2′-bipyridine in the case of the selenocyanate complexes. Hence, the $d\pi-\pi_1$(bpy) MLCT bands in both $[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$ and $[(bpy)_2Ru(NCSe)Cl]\cdot 2H_2O$ are observed at slightly higher energies compared to those of the analogous thiocyanate[11] compounds (515 and 502 nm, respectively, for $[(bpy)_2Ru(NCS)_2]$ and $[(bpy)_2Ru(NCS)Cl]$).[30]

However, the greater π back-bonding in the [M–NCSe] unit than that in the [M–NCS] unit could not be explained satisfactorily on the basis of the energies of the $3\pi^*$-acceptor orbitals[14] of the chalcogenocyanate ions. The difference between the energies of the $3\pi^*$ orbitals of cyanate and thiocyanate is very small,[14] approximately 60 cm^{-1}. A similar trend can be applicable for the selenocyanate ion, which essentially means that the energy and symmetry[16] of these orbitals should give similar π-bonding properties for both thiocyanate and selenocyanate ions. Notwithstanding these ambiguities, the greater π interaction in selenocyanate compounds than that in thiocyanate compounds leads to several important consequences such as (i) the larger stability of the selenocyanato-bridged mixed-valence compounds compared to that of the thiocyanato-bridged ones,[10,11] (ii) the smaller quantum yields for the emission in selenocyanate compounds compared to those for thiocyanate compounds, and (iii) the relatively larger enhancement of the bipyridine bands in the RR spectra of the selenocyanate complexes than in those of the corresponding thiocyanate complexes.

The resonance Raman spectra of the selenocyanate compounds show, in general, a greater resonance enhancement of the various bands of the coordinated 2,2′-bipyridine compared to those of the thiocyanate compound. The excitation of the compounds within the lowest energy MLCT profile yields the characteristic bands due to the vibrational modes of the coordinated 2,2′-bipyridine, albeit with markedly varying intensities.[31] However, the excitations of the monomeric and dimeric compounds at 457.9 and 514.5 nm, respectively, yield the resonance enhancement of the ν(CN) band of the selenocyanate group. This is in concordance with the assignment of the bands and shoulders in the visible region of the electronic spectrum.

It has been observed recently[32] for several diimine-bridged binuclear bis(bipyridine)ruthenium(II) compounds that the π^* orbitals on the briding ligands and the 2,2′-bipyridine coligands are widely separated and the visible region of their electronic spectra shows two intense bands due to the MLCT transitions that are terminating on the π^* orbitals of the bridging ligands and the 2,2′-bipyridine coligands. Excitation within these different bands using Ar ion laser and dye laser lines shows the resonance enhancement of the corresponding vibrational modes, thereby providing the means for an unambiguous assignment of the bands. Such an exercise was not possible with the chalcogenocyanato-bridged compounds, as the MLCT transitions terminating on the $3\pi^*$ orbitals of the NCX^- ions and the π^* orbitals of 2,2′-bipyridine are strongly overlapping, as seen from the strongly overlapping bands due to M → bpy and M → NCSe charge transfer.

The shoulder corresponding to the M–NCSe MLCT is red-shifted by about 3500 cm^{-1} in the dimer from that of the monomer. This red shift is attributed to the π interaction present in the [M–NCSe–M] unit via the bridge. However, the interaction through the selenocyanate bridge seems to be only moderate, in light of the diimine-bridged binuclear complexes discussed earlier,[32] where a red shift of ~8000 cm^{-1} for the $d\pi-\pi^*$ (bridge) transition has been observed, showing a large stabilization of the π^* orbital of the bridging diimines. Other evidence for the interaction through the selenocyanate bridge is obtained from the quantum yields of the emission for the monomer and dimer. The emission in the dimeric compound is approximately 10-fold less than that in monomer. The partial quenching of the emission in the dimer can be attributed to the coordination of the second $[(bpy)_2Ru]^{n+}$ unit on the free Se end of $[(bpy)_2RuCl(NCSe)]\cdot 2H_2O$. The electron-withdrawing nature of this second $[(bpy)_2Ru]^{n+}$ unit via the selenocyanate bridge could lead to an efficient pathway for a nonradiative deactivation[11,32] of the emissive state. Further, the selenocyanate-bridged dimer is an approximately 50-fold weaker emitter compared to the thiocyanate-bridged dimer.[11] This is in conformity with the slightly stronger π interaction through the selenocyanate bridge than through the thiocyanate bridge, and the pathway for the nonradiative deactivation of the emissive state is more efficient in the case of $SeCN^-$ compound compared to that of the SCN^- compound.

The ligand-bridged mixed-valence compounds of $[(CN)_5Fe]^{n-}$ and $[(bpy)_2Ru]^{n+}$ building blocks seldom show[10,13] a delocalized limit for the optical electron (Robin and Day class III behavior), while most of the class III compounds described till now[13] have the $[(NH_3)_5Ru]^{n+}$ building block, where the "spectator ligands" are purely σ-donor moieties. The extent of delocalization of the optical electron in a given mixed-valence compound is controlled both by the bridging and the nonbridging ligands.[11,15,33] The smaller amount of delocalization in the cases of $[Cl(bpy)_2Ru(\mu\text{-}L)Ru(bpy)_2Cl]^{n+}$, $[(CN)_5Fe(\mu\text{-}L)Fe(CN)_5]^{n-}$, and $[(CN)_5Ru(\mu\text{-}L)Ru(CN)_5]^{n-}$ compared to that of $[(NH_3)_5Ru(\mu\text{-}L)Ru(NH_3)_5]^{n+}$, for any bridging ligand L, could be explained by the degree of metal–metal interaction. If the nonbridging ligands that surround the metal center are strongly π-acidic, they compete favorably with the bridging ligands to interact with the $d\pi$ orbitals of the metal center. Thus, cyanide or 2,2′-bipyridine ligands act as the withdrawing groups of the $d\pi$ electrons from the metal centers, and the $d\pi$ orbitals are considerably lower in energy compared to those of the ammonia ligands.[33-35] In light of the foregoing arguments, if one sees the delocalization of the optical electron in the chalcogenocyanato-bridged mixed-valence compounds,[9-11] the gradual decrease in the extent of delocalization, from

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(30) Although the $E_{1/2}$ values for the Ru(2+/3+) couple are almost the same for the complexes $[(bpy)_2Ru(NCSe)_2]\cdot 2H_2O$ and $[(bpy)_2RuCl_2]\cdot 2H_2O$ (0.32 and 0.29 V, respectively), the former exhibited the $d\pi-\pi_1$(bpy) MLCT band at considerably higher energy, i.e., at 493 nm compared to that of the latter, 552 nm. This could be explained on the basis of the π-acidic nature of the selenocyanate ion vis-à-vis the π-basic nature of the chloride ion.

(31) Balk, R. W.; Snoeck, T.; Stufkens; Oskam, A. *Inorg. Chem.* **1980**, *19*, 3015.

(32) Fuchs, Y.; Lofters, S.; Dieter, T.; Shi, W.; Morgan, R.; Strekas, T. C.; Gafney, H. D.; Baker, A. D. *J. Am. Chem. Soc.* **1987**, *109*, 2691 and references therein.

(33) Shepherd, R. E.; Johnson, C. R. *Inorg. Chem.* **1983**, *22*, 1117, 2439. The qualitative MO diagram used in these papers for $[(CN)_5Ru(pyz)]^{3-}$ and $[(NH_3)_5Ru(pyz)]^{2+}$ shows the reduced interaction of $[(CN)_5Ru]^{n-}$ unit with the π^*(pyz) orbital.

(34) (a) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94. (b) Yeh, A.; Haim, A.; Tanner, M.; Ludi, A. *Inorg. Chim. Acta* **1979**, *33*, 51.

(35) The absence of IT bands in the mixed-valence complexes $[M(CN)_5pyzRu(NH_3)_5]$, where M = Ru[15] or Fe,[34b] has been explained along these lines.

$[(NH_3)_5Ru]^{n+}$ to $[(CN)_5Fe]^{n-}$ to $[(bpy)_2Ru]^{n+}$, is understandable. Thus, it seems, one could conveniently modify the metal–metal interaction by choosing the appropriate nonbridging "spectator ligands". This will have a large impact on the biological electron-transfer processes where the driving force (a function of redox asymmetry) plays an important role.[36]

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Registry No. $[(bpy)_2Ru(NCSe)_2]$, 115794-05-3; $[(bpy)_2Ru(NCSe)Cl]$, 115704-98-8; $[(bpy)_2Ru(SeCN)Cl]$, 115704-99-9; $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl]BPh_4$, 115705-03-8; $[(bpy)_2Ru(NCSe)Cl]BPh_4$, 115705-01-6; $[(bpy)_2Ru(NCSe)(SeCN)]BPh_4$, 115731-26-5; $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl](BPh_4)_3$, 115705-05-0; $[Cl(bpy)_2RuNCSeRu(bpy)_2Cl](BPh_4)_2$, 115705-07-2; $[(bpy)_2Ru(NO)Cl](PF_6)_2$, 58575-12-5; *cis*-$[(bpy)_2RuCl_2]$, 19542-80-4; potassium azide, 20762-60-1.

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(36) Isied, S. S. *Prog. Inorg. Chem.* **1984**, *32*, 443.

(37) One of the reviewers has suggested that this could be a trans isomer on the basis of IR spectral evidence presented in a manuscript that is under editorial consideration. However, we feel IR spectral evidence alone would prove insufficient for the correct assignment of the isomer. ^1H NMR spectral study for this compound, which is presently being undertaken in our laboratory, might solve this problem, and this will form the basis for a future paper.

Contribution from the Department of Chemistry, 6-331,
Massachusetts Institute of Technology, Cambridge, Massachusetts 02139

Preparation and Characterization of Two Unsubstituted Hydrazido(1–) Complexes, $W(\eta^5\text{-}C_5Me_5)Me_4(\eta^2\text{-}NHNH_2)$ and $[W(\eta^5\text{-}C_5Me_5)Me_3(\eta^2\text{-}NHNH_2)]^+[SO_3CF_3]^-$

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Received February 17, 1988

The reaction between $[WCp^*Me_4]^+$ and 4 equiv of hydrazine (2-equiv excess) yields thermally unstable $WCp^*Me_4(NHNH_2)$. Crystals of $WCp^*Me_4(NHNH_2)$ obtained from a mixture of pentane and THF retain 1 equiv of THF per metal at low temperature, the THF being bonded to two NH_2 protons in a symmetrically bound η^2-$NHNH_2$ ligand in one of the two $WCp^*Me_4(NHNH_2)$ molecules in each asymmetric unit. Evaluation of the potential hydrogen bonds between the two molecules in the asymmetric unit allows us to conclude that the lone pair on the pyramidal NH nitrogen atom is pointing toward the Cp* ligand. (Crystal data: $a = 15.100$ (7) Å, $b = 16.551$ (6) Å, $c = 8.860$ (8) Å, $\alpha = 97.26$ (6)°, $\beta = 100.92$ (5)°, $\gamma = 66.08$ (4)°, $V = 1984.4$ Å^3, space group $P\bar{1}$, $Z = 4$, $M_r = 410.31$, ρ(calcd) = 1.564 g cm^{-3}, $\mu = 55.4$ cm^{-1}. Final $R_1 = 0.0973$ and $R_2 = 0.1153$.) ^1H and ^{15}N NMR studies show that two of the three hydrazido(1–) protons equilibrate first, probably by a shift to the lone pair on the NH nitrogen atom of the NH_2 proton that points toward the Cp* ligand. $WCp^*Me_4(NHNH_2)$ loses methane in an apparent first-order decomposition reaction to give $WCp^*Me_3(NNH_2)$ in high yield. Protonation of $WCp^*Me_3(NNH_2)$ yields $[WCp^*Me_3(NHNH_2)]^+$, a structure study of which showed it also to contain an η^2-$NHNH_2$ ligand, but one that is unsymmetrically bound with the NH nitrogen atom being sp^2 hybridized. (Crystal data for the triflate derivative: $a = 23.619$ (4) Å, $b = 8.486$ (2) Å, $c = 21.921$ (6) Å, $\beta = 100.40$ (2)°, $V = 4321$ (3) Å^3, space group $C2/c$, $Z = 8$, $M_r = 544.28$, ρ(calcd) = 1.78 g cm^{-3}, $\mu = 57.9$ cm^{-1}. Final $R_1 = 0.049$ and $R_2 = 0.059$.) $WCp^*Me_4(NHNH_2)$ is protonated to give what is postulated to be an η^2-hydrazine complex, $[WCp^*Me_4(NH_2NH_2)]^+$, with a structure closely related to that of $WCp^*Me_4(NHNH_2)$.

Introduction

It is generally believed (although there is no direct evidence) that dinitrogen is activated by and reduced at a molybdenum center in nitrogenase, with the possible assistance of a second metal (most likely Fe).[1] For this reason the coordination of molecular nitrogen to one or more transition metals and its reduction to ammonia have been the subject of a great deal of research in the past 2 decades.[1d] The long-term goals are to understand the inorganic chemistry at metal centers in nitrogenases[1f] and to design a nonbiological catalytic system for the reduction of dinitrogen under mild conditions, ideally 25 °C and 1 atm.

One of the possible intermediates in a sequence of steps that could lead to reduction of dinitrogen at a single metal center (eq 1) is a hydrazido(1–) complex, M–$NHNH_2$. A complex that

$$M\text{—}N_2 \xrightarrow[2e^-]{2H^+} M\text{—}N_2H_2 \xrightarrow[e^-]{H^+} M\text{—}NHNH_2 \xrightarrow[e^-]{H^+(N_\beta)} M\text{=}NH + NH_3 \quad (1)$$

almost certainly contains the hydrazido(1–) ligand has been reported,[2] but unfortunately it could not be characterized fully. In contrast, there are a great many reports of complexes that contain substituted hydrazido(1–) ligands, M–NRNR′R″.[1d] We reported in a preliminary communication[3] that the reaction between $[WCp^*Me_4]^+$ and hydrazine yielded what was believed to be $WCp^*Me_4(NHNH_2)$, a species that readily loses methane to give $WCp^*Me_3(NNH_2)$, from which $[WCp^*Me_3]_2(\mu\text{-}N_2)$[3,4] could be prepared by addition of $[WCp^*Me_4]^+$. Since then we have found that both $WCp^*Me_4(NHNH_2)$ and $WCp^*Me_3(NNH_2)$ can be protonated, the former to give $[WCp^*Me_4(NH_2NH_2)]^+$ and the latter to give a second example of a hydrazido(1–) complex, $[WCp^*Me_3(NHNH_2)]^+$. The results of these studies are reported here.

Results

Preparation and Characterization of $WCp^*Me_4(NHNH_2)$. Addition of $[WCp^*Me_4]^+$ ($Cp^* = \eta^5\text{-}C_5Me_5$; the anion is usually PF_6^-) to an excess (4 equiv) of hydrazine in diethyl ether results

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(1) (a) Coughlin, M., Ed. *Molybdenum and Molybdenum-Containing Enzymes*; Pergamon: Elmsford, NY, 1980. (b) Hardy, R. W. F., Bottomley, F., Burns, R. C., Eds. *A Treatise on Dinitrogen Fixation*; Wiley-Interscience: New York, 1979. (c) Gibson, A. H., Newton, W. F., Eds. *Current Perspectives in Nitrogen Fixation*; Elsevier: Amsterdam, 1981. (d) Henderson, R. A.; Leigh, J.; Pickett, C. J. *Adv. Inorg. Chem. Radiochem.* **1983**, *27*, 197. (e) For a discussion of the most recent theories see: Conradson, S. D.; Burgess, B. K.; Newton, W. E.; Mortenson, L. E.; Hodgson, K. O. *J. Am. Chem. Soc.* **1987**, *109*, 7507. (f) Recent genetic evidence implicates FeMo-co as the site of binding and reduction of dinitrogen.[1g] Nitrogenases that contain vanadium[1h] or tungsten[1i] are now known. (g) Hawkes, T. R.; McLean, P. A.; Smith, B. E. *Biochem. J.* **1984**, *217*, 317. (h) Morningstar, J. E.; Hales, B. J. *J. Am. Chem. Soc.* **1987**, *109*, 6854. (i) Hales, B. J.; Case, E. E. *J. Biol. Chem.* **1987**, *262*, 16205.

(2) McCleverty, J. A.; Rae, A. E.; Wolochowicz, I.; Bailey, N. A.; Smith, J. M. A. *J. Chem. Soc., Dalton Trans.* **1983**, 71.

(3) Murray, R. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1985**, *107*, 4557.

(4) Churchill, M. R.; Li, Y. J. *J. Organomet. Chem.* **1985**, *301*, 49.

0020-1669/88/1327-3574$01.50/0