Ru^{II}[(2,2'-bpy)$_2$(NCS)$_2$]: Evidence for a Trans Configuration of the Rigorously Desolvated Complex

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A detailed temperature-dependent FTIR examination of the compound Ru^{II}[(2,2'-bpy)$_2$(NCS)$_2$], prepared from *cis*-Ru^{II}[(2,2'-bpy)$_2$(Cl)$_2$] by metathesis to a bis(acetonitrile) intermediate and subsequent photochemical conversion to the thiocyanate complex, shows that the rigorously desolvated title compound adopts a (slightly distorted) trans octahedral configuration. This assignment is consistent with the Raman spectrum of the Ru complex, as well as with comparison of variable-temperature IR data for *trans*-M[(py)$_4$(NCS)$_2$] [M = Mn(II), Co(II), Ni(II)], *cis*-Ru[(2,2'-bpy)$_2$(CN)$_2$], and the previously reported spin-crossover compound *cis*-Fe^{II}[(2,2'-bpy)$_2$(NCS)$_2$]. The available spectroscopic data suggest that the N-bonded thiocyanate title complex is low-spin over the temperature range $79 < T < 300$ K.

Introduction

The chemistry of the complexes of ruthenium(II) has received increasing attention in the recent literature, in part because of the usefulness of such compounds as models in the study of a variety of dynamic chemical processes, including optical excitation and relaxation,[1] electron transport,[2] and bonding and conformational changes in solution of such species.[3] In particular, the neutral complexes of the type Ru^{II}[(L$_2$)(X)$_2$], where L is a bidentate, nitrogen-bonding ligand, such as 1,10-phenanthroline (phen) or 2,2'-bipyridyl (bpy), and X is an appropriate monovalent anion, have been reported in detail,[4] due to the interest in their intrinsic properties, as well as their usefulness as precursors for further metathetical processes. In this context, the preparation of a number of bis(bipyridyl) complexes of Ru(II) has been reported.[5] A common starting point for the preparation of such complexes with X = NO$_3^-$, ClO$_4^-$, NCS$^-$, and NO$_2^-$ has been the commercially available Ru[(bpy)$_2$(Cl)$_2$]. This compound is assumed[6,7] to have the two halogen ligands occupying cis positions in a distorted octahedral environment around the metal atom, and it was reasonable to assume that replacement of the chlorides by other monovalent anions would likewise result in a cis octahedral configuration. In this context, it is interesting to note that Godwin and Meyer,[7] in their study of Ru^{II}[(bpy)$_2$(NO)Cl](PF$_6$)$_2$, have shown that the ^{1}H NMR spectrum of the nitrosyl complex is inconsistent with a trans arrangement of the two monodentate ligands and have thus ascribed a cis configuration to this complex, derived from the same starting material as the title compound. To elucidate the configuration of the X = NCS complex, the title compound was studied in detail, and inferences concerning its structure are reported in the present investigation.

Experimental Section

(a) Preparations. Ru[(bpy)$_2$(NCS)$_2$]. This compound was prepared by literature methods[8] involving initial conversion of the dichloride (ob-

tained as the dihydrate from Strem Chemical Co.) to the bis(acetonitrile) complex and subsequent photolysis of the PF$_6$ salt in the presence of excess NH$_4$SCN in acetone. The product so obtained was purified by adsorption onto an alumina column, with CH$_2$Cl$_2$ as solvent, and subsequent elution with 80% CH$_2$Cl$_2$/acetone. The resulting product, exhaustively desolvated by vacuum-drying at room temperature, was characterized by elemental analysis, UV–vis, infrared (vide infra), and Raman spectroscopies, and electrochemical procedures. Despite extensive experimentation, it has not proven possible so far to grow diffraction-suitable single crystals of this compound in the absence of mother liquor. Crystals obtained from the slow evaporation of a DMSO solution, which are then vacuum-dried, turn out to be either twinned or fractured and give rise to broad diffraction peaks unsuitable for detailed crystallographic study. It is interesting to note, however, that the KBr infrared spectra of such crystals are indistinguishable from those obtained from the microcrystalline reaction products resulting from the synthetic procedure referred to. The UV–vis spectra of the samples examined in the present study were found to be in excellent agreement with the data reported in the literature.[1]

M[(py)$_4$(NCS)$_2$] [M = Mn(II), Co(II), Ni(II)]. These compounds were prepared as microcrystalline solids by using literature methods[9] and dried at room temperature under vacuum. Single crystals of the Ni(II) complex, suitable for X-ray diffraction, were obtained by an aqueous diffusion process at room temperature. These samples were characterized by infrared (vide infra) and powder diffraction methods. The latter study, carried out with a Scintag PADV diffractometer (Cu Kα radiation, single-crystal Ge detector) at room temperature, showed unambiguously that the Co(II), Ni(II), and Mn(II) compounds are isomorphous and isostructural. The isomorphous nature of the Co(II) and Ni(II) compounds was demonstrated in an early single-crystal diffraction study,[10] but the absence of absorption corrections and the use of film methods cast some uncertainty on these results. To the best of our knowledge, no precision single-crystal diffraction study of the Ni(II) compound has been reported in the recent literature.

Ru[(bpy)$_2$(CN)$_2$] was prepared by the method of Schilt[11a] and purified by the chromatographic procedure of Crosby et al.[11b] to yield a bright red microcrystalline product, which was characterized by IR techniques.

(b) Infrared Spectroscopy. Variable-temperature infrared spectra of the title compound and related complexes were obtained by using the experimental techniques discussed earlier,[12–14] employing a nitrogen-purged IBM IR 32 midrange spectrometer fitted with KBr optics, as well as a Mattson Cygnus-100 spectrometer at room temperature. All samples were studied as solids in vacuum-compressed KBr pellets at levels of ~1% by weight. The CN stretching frequency of the thiocyanate ligand was treated as a single absorbance peak (see the detailed discussion below), and the temperature dependence of the band center was calculated from an (assumed) second-order polynomial fitting routine, by using the POLYCALC program described earlier.[15]

(c) Raman Spectroscopy. Raman spectra at room temperature were obtained by using a 488-nm excitation source (Ar$^+$) on samples pressed into a rotating disk sample holder, with the use of a Spex double-

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Table I. Summary of Infrared Results (cm^{-1})

	Co[(py)$_4$(NCS)$_2$]	Ni[(py)$_4$(NCS)$_2$]	Mn[(py)$_4$(NCS)$_2$]	Fe[(bpy)$_2$(NCS)$_2$]	Ru[(bpy)$_2$(NCS)$_2$]
conformation	trans	trans	trans	cis	trans
ν_{CN}(300 K)	2073.7 (17.5)^a	2082.9 (20.3)	2061.9 (20.1)	2067.8, 2060.4 ($\sim$10)^b	1100.3 (28.6)
ν_{CN}(79 K)	2078.6, 2074.7 (sh) (19.0)	2089.2, 2084.3	2064.7 (23)	2118.5, 2110.8 ($\sim$7)^c	2106.5 (28.2)
ν_{CS}(300 K)	802	801	798	799	801
ν_{CS}(79 K)	801	801	799	799	800
δ_{NCN}(300 K)	482	482	482	d	d
δ_{NCN}(79 K)	482, 478	481	481	d	d

^{a} The parenthetical value is the full width at half-maximum of the absorption line, treated as a single maximum. ^{b} The symmetric and asymmetric CN stretches of the high-spin (HS) form. ^{c} The symmetric and asymmetric CN stretches of the low-spin (LS) form. ^{d} Not observed.

monochromator spectrometer. A slit width of 6 cm^{-1} and a scanning rate of 2 s cm^{-1} over the range 1900–2200 cm^{-1} afforded optimal signal-to-noise characteristics in the resultant data. Analysis of the samples by electrochemical means (vide infra) both before and after the Raman spectral study confirmed the absence of photochemical decomposition by the irradiating laser source.

(d) Electrochemistry. Cyclic voltammetry of the title compound was carried out in CH$_3$CN solution (0.1 M tetraethylammonium perchlorate as supporting electrolyte) under standard conditions (Pt-disk electrode). The reference electrode was Ag, and the data were adjusted to SSCE with ferrocene used as an internal standard. A single wave with a 2+/3+ potential of +0.64 V was observed and is in good agreement with published values. The electrochemical data were used to establish the chemical purity of the product resulting from the synthetic procedure, as well as to confirm the absence of photochemical decomposition during the Raman spectral examination of the title compound.

Results and Discussion

(a) The Thiocyanate CN Stretch. The most intense infrared-active absorbance of the title compound is due to the ν_1 mode of the SCN ligand. The relevant portion of the midrange spectrum of the title compound is shown in Figure 1. On first inspection of the data, this mode appears to be a single band at $\sim$2100 cm^{-1}. The fact that the well-studied homologue[14,16] Fe^{II}[(2,2'-bpy)$_2$-(NCS)$_2$], which is known to adopt a distorted cis octahedral configuration in the solid, shows two CN absorptions at 2068 and 2061 cm^{-1} (Figure 1b) leads directly to the hypothesis that the title compound is, in fact, a trans octahedral complex. In perfect trans symmetry, the mutual exclusion principle demands that the *asymmetric stretch* be infrared active and the *symmetric* stretch be observable only in the Raman spectra. The infrared data thus strongly suggested that the *cis*-dichloro starting material had, in fact, been converted to a trans conformation for the thoroughly desolvated complex during the synthetic procedure and subsequent sample treatment.

This interpretation is further supported by the infrared data for the related bis(cyano) compound reported earlier by Schilt.[11a] The CN stretching region of the IR spectrum of this compound, obtained by elution of the rigorously purified reaction product from a silica-gel column, using CH$_3$OH as eluent, shows two well-resolved absorbance maxima at 2072.9 and 2059.5 cm^{-1} at 295 K. On the basis of the earlier IR data, Schilt assigned a cis structure to this complex, and these results were subsequently confirmed by the chromatographic work of Crosby et al.[11b] These authors reasoned that the presence of a permanent dipole in the cis structure would lead to a smaller R_f value than for the chromatographic behavior of the corresponding trans compound and concluded that the material eluted from silica-gel and alumina columns using CH$_3$OH and CH$_3$OH/CHCl$_3$ was the cis isomer of Ru[(bpy)$_2$(CN)$_2$]. The band position of the two CN stretching modes has been found to be essentially temperature independent (within 1 cm^{-1}) over the range 79 < T < 300 K.

Because the CN stretch is observed in a spectral region that is free of interferences by other bands, it is possible to subject the IR absorbance data of the title compound to a second-order polynomial regression analysis, with the assumption that the band shape is governed by a Lorentzian distribution. Such an analysis, in fact, showed the band to be asymmetric and to have a full width
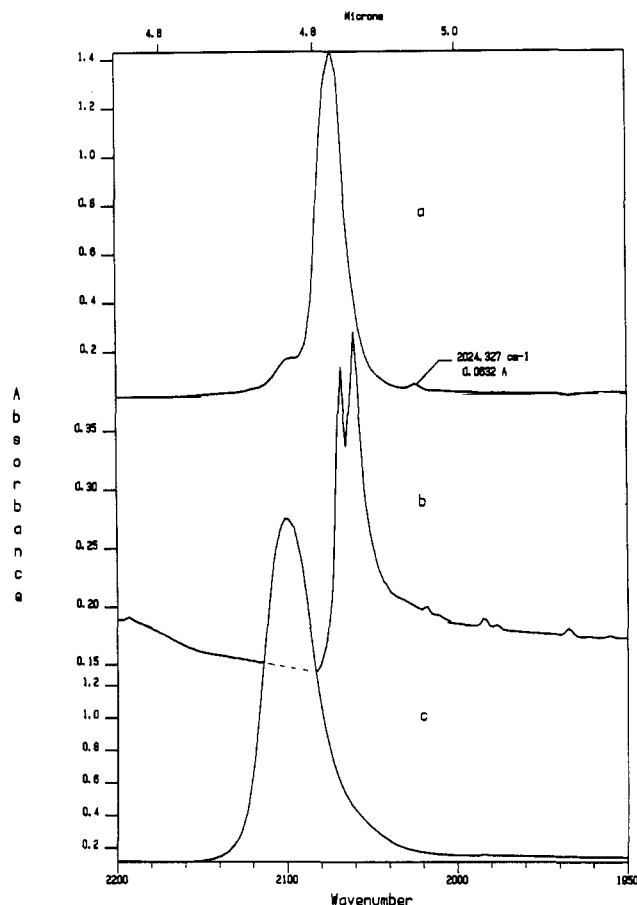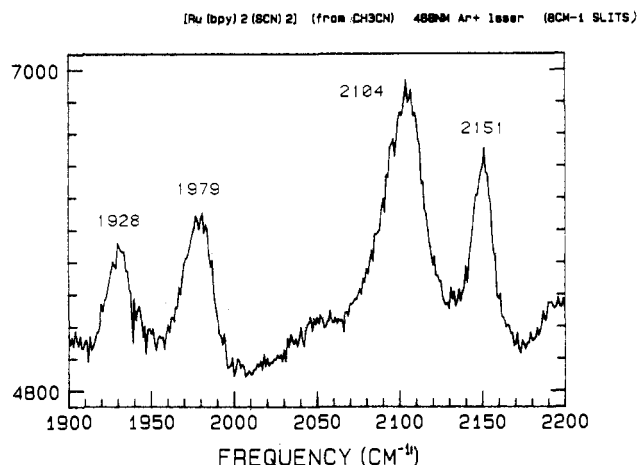
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Figure 1. Portion of the midrange IR spectrum in the ν_1 region. (a) Co[(py)$_4$(NCS)$_2$] in KBr. The small feature at 2024 cm^{-1} is the ^{13}C component of the CN stretch. This compound is in the HS configuration in the range 300 > T > 77.3 K.[22] (b) Fe[(bpy)$_2$(NCS)$_2$] as a Kel-F mull on KBr. A significant Christiansen effect is observed due to the refractive index mismatch of the dispersant, which is needed to permit observation of the ordered spin state. The two components of the CN stretch due to the cis configuration of the complex in its HS form are clearly resolvable from the data. (c) Ru[(bpy)$_2$(NCS)$_2$] in KBr. The full width at half-maximum of this absorbance is $\sim$29 cm^{-1}.

at half-maximum of about 29 cm^{-1}, compared to a typical value of $\sim$10–12 cm^{-1} for well-documented single CN stretching bands (as for example in the corresponding Fe(II) complex). The relevant data are summarized in Table I. It has been suggested that the broad IR absorbance in the case of the Ru complex arises from the existence of *isotopomers* due to the presence of seven stable Ru isotopes (five with an abundance greater than 12%). This hypothesis is currently being pursued by IR studies using isotopically labeled samples. The temperature-dependence data for the title compound, over the range 79 < T < 300 K, show the usual blue shift as the temperature is lowered. The data are reasonably well represented by a function of the form $\nu_{CN} = 2104.9 + 6.6 \times 10^{-3}T - 5.4 \times 10^{-5}T^2$ cm^{-1} (where T is the Kelvin temperature).

An examination of the IR spectrum of the intermediate complex, Ru[(bpy)$_2$(CH$_3$CN)$_2$](PF$_6$)$_2$,[17,18] showed a medium strong

Figure 2. Portion of the room-temperature Raman spectrum of Ru-[(bpy)$_2$(NCS)$_2$] in the CN stretching mode region. Cyclic voltammograms taken before and after the spectral data acquisition confirm the absence of significant photochemical decomposition of this sample (4880-Å irradiation). The spectral features at 1979 and 2151 cm^{-1} are ascribed to a (bpy) vibrational mode.

absorbance at 2283 cm^{-1} (coordinated acetonitrile) and a weaker band at 2253 cm^{-1} (occluded solvent?). The former is completely absent in the IR spectrum of the title compound, evidencing complete substitution of CH$_3$CN by NCS$^-$, as expected. The IR data of the intermediate are, however, not adequate to assign a cis or trans configuration to this solid, so that these data are insufficient to permit a conclusions as to which step of the synthetic procedure is primarily involved in the cis to trans conversion. The partial conversion of *cis*-Ru[(bpy)$_2$(Cl)$_2$] to the trans form in the context of a synthetic procedure has been discussed by Krause.[8]

The Raman spectrum of the title compound shows a moderately strong scattering maximum at ~2105 ± 2 cm^{-1} (Figure 2), and the question immediately arises whether this is the "missing" symmetric CN stretch associated with an ideal trans configuration. To answer this question, a number of related transition-metal complexes have been examined by the infrared methods referred to above. In particular, it is appropriate to consider the results for the compound Co^{II}[(py)$_4$(NCS)$_2$], since a precision single-crystal structure determination has been reported by Hartl and Brudgam[19] for this complex. The Co(II) compound was found to crystallize in the monoclinic space group $C2/c$ with 4 formula units per unit cell, with the two NCS$^-$ ligands occupying trans positions around the metal center. The structure does not have identically an inversion symmetry, since the N(py)–Co–N(NCS) bond angles are 88.87 (9) and 89.48° and the NCS ligand has an internal angle of 179.2 (2)°. The room-temperature IR spectrum (Figure 1a) shows an absorption maximum at 2073.7 cm^{-1}, with a shoulder at about 4 cm^{-1} lower frequency. On cooling to 79 K, these bands do not become better resolved but are blue-shifted by about 5 cm^{-1}. The room-temperature Raman spectrum of this compound shows a single sharp band at 2074 ± 1 cm^{-1} in the CN stretching region.

In the case of the corresponding Ni^{II}[(py)$_4$(NCS)$_2$] complex, the strong, nearly symmetric absorption maximum is observed at 2082.8 cm^{-1}. On cooling to 79 K, this feature is clearly resolvable into a strong absorbance at 2089.2 cm^{-1}, with a weaker maximum at 2084.3 cm^{-1}. The early single-crystal X-ray diffraction data[11] for this compound show a bond angle of 165° for the Ni–N–CS bond, with an otherwise "linear" NCS ligand. The space group of this compound was again refined as $C2/c$. Finally, it should be noted that the analogous Mn(II) compound gives rise to a strong absorbance at 2061.9 cm^{-1}, that is, some 12 wavenumbers lower than the Co(II) homologue, but otherwise the IR

spectra bear a very close resemblance. Although the powder pattern data for the Co(II), Ni(II), and Mn(II) complexes strongly suggest an isomorphous and isostructural relationship among the three compounds, it should be emphasized that (to the best of our knowledge) high-precision single-crystal diffraction data have only been reported for the cobalt member of the series.

(b) The CS Stretch and NCS Bending Modes. In addition to the large oscillator strength ν_1 fundamental, the SCN group has two other modes that have frequently been considered diagnostic[20] with respect to the ligating behavior of this moiety: namely the CS stretch at about 800 cm^{-1} and the bending mode at about 480 cm^{-1}. In the "free" NCS$^-$ ion, these two absorbances are observed at ~480 and 746 cm^{-1}. As Bailey et al.[20] have pointed out in their extensive review of the relevant IR data, N-coordination increases the frequency of the ν_3 mode, as is noted in the present data, whereas S-coordination has the opposite effect on the contribution of the dominant resonance form. For the tetrakis(pyridine) compounds, both these modes are readily identified in the spectra, and the relevant data are summarized in Table I. In the case of the title compound, there is a relatively weak feature at 802.9 cm^{-1} that is absent in the KBr spectrum of 2,2'-bpy, which can be reasonably assigned to the CS stretching mode (Table I), but the bending mode cannot be identified in the room-temperature spectra. The same observation is made for Fe[(bpy)$_2$(NCS)$_2$] (cis), for which weak, broad absorbances are seen at 799 cm^{-1} but for which the NCS bending mode has not been identified in the spectra.

The above data suggest very strongly, that the following conclusions appear to be justified: (a) The thiocyanate ligand in the rigorously desolvated title compound is N-bonded, as has been reported for the corresponding Fe(II) spin-crossover complex (and its SeCN homologue), as well as for the M(py)$_4$(NCS)$_2$ complexes discussed above. (b) The ν_1 fundamental CN stretching frequency in the Ru(II) complex is red-shifted by ~15 cm^{-1} from the low-spin absorbance of the corresponding Fe(II) compound (but blue-shifted by ~35 cm^{-1} from the high-spin form of this complex), suggesting that the Ru(II) compound is low-spin over the temperature range 79 < T < 300 K, as expected from the increased $10Dq$ value for 4d^6 complexes as compared to that of their 3d^6 partners. The early crystallographic study, referred to above, as well as extensive susceptibility data,[22] shows that the Co^{II}-[(py)$_4$(NCS)$_2$] complex is high-spin at room temperature (μ_{eff} = 4.84 μ_B, S = $^3/_2$). The thiocyanate CN stretch for this HS complex is observed at ~2074 cm^{-1} (Table I), that is ~26 cm^{-1} red-shifted with respect to the analogous absorbance of the title compound. It should be borne in mind, however, that the spin state on the metal atom cannot be elucidated solely from the position of the thiocyanate ν_1 band per se. This follows from the IR data[14] for the polymer Fe[(bpy)(NCS)$_2$], which had been shown by Dockum and Reiff[21] to have μ_{eff} = ~5 μ_B at 300 K and ~0.88 μ_B at 1.39 K, without evidencing any crossover behavior. However, in the present case, the diamagnetism of the title compound over the temperature range 6 < T < 300 K has been further confirmed by SQUID susceptometer measurements on samples of the rigorously desolvated complex. In addition, ^{1}H and ^{13}C NMR spectra of samples in DMSO confirm the nonparamagnetic nature of Ru[(bpy)$_2$(NCS)$_2$] in solution at room temperature. In this context, it is also worth noting that increased metal-to-ligand back-donation, which involves the t$_{2g}$ orbitals of the LS form of the Fe(II) crossover compound, contributes to a blue shift of ~50 cm^{-1}. Evidently, in the *trans*-Ru[(bpy)$_2$(NCS)$_2$] compound of the present study, this effect on the ν_1 mode of the ligand is somewhat reduced. (c) The near degeneracy of the *symmetric* and *asymmetric* CN stretching frequencies is consistent with a

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trans configuration of the two thiocyanate ligands, but the broadness of the IR absorbance, as well as the small (but real) displacement of the Raman absorbance maximum from the position of the IR absorbance, leads to the not unexpected conclusion that ideal D_{2h} symmetry does not obtain, presumably due (in part) to the nonlinearity of the NCS ligand.

The structural inferences summarized above would seem to be important with respect to devising synthetic strategies involving Ru complexes that are intended for use as model compounds in a variety of physicochemical studies. In particular, the use of such complexes in the study of electron-transport processes in model systems having biological significance is being actively pursued in these laboratories. A clearer understanding of the stereochemistry of these materials would appear to be crucial in the pursuit of such studies.

Note Added in Proof. After the completion of this study, it proved possible to grow diffraction-suitable single crystals from both CH_3CN and $(CH_3)_2SO$ solutions. In the presence of mother liquor, these crystals contain one molecule of solvent per metal atom and adopt a configuration in which the two SCN ligands are cis to each other. The details of these crystallographic studies are to be published.[23]

(23) Herber, R. H.; Nan, G.; Potenza, J.; Schugar, H. J.; Bino, A., to be submitted for publication.

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Structures of Three Novel Polynuclear Oxo- and Sulfidomolybdenum Complexes Containing the Hydrotris(3,5-dimethyl-1-pyrazolyl)borate Ligand

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The complexes $[\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoO(\mu\text{-}OH)]_2$ (1), $[\{HB(Me_2pz)_3\}MoO]_2(\mu\text{-}O)(\mu\text{-}S_2)$ (2), and $\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoS(S_2CNEt_2)$ (3) have been isolated and characterized by X-ray crystallography. $1 \cdot 3C_2H_4Cl_2$ crystallizes in the triclinic space group $C\bar{1}$ with $a = 18.421$ (3) Å, $b = 10.547$ (3) Å, $c = 15.575$ (4) Å, $\alpha = 90.07$ (2)°, $\beta = 104.76$ (2)°, $\gamma = 90.53$ (2)°, and $Z = 2$. Each linear tetranuclear complex possesses $\bar{1}$ symmetry. $2 \cdot {}^1/_2 C_6H_6$ crystallizes in monoclinic space group $P2_1/n$ with $a = 15.126$ (1) Å, $b = 14.364$ (2) Å, $c = 20.145$ (2) Å, $\beta = 105.835$ (7)°, and $Z = 4$. Complex 2 contains a rare mode of cis end-on disulfide bridge in which each molybdenum is coordinated to a different sulfur atom of the S_2^{2-} ligand. $3 \cdot {}^2/_3 CH_2Cl_2$ crystallizes in the triclinic space group $P\bar{1}$ with $a = 12.103$ (3) Å, $b = 16.107$ (4) Å, $c = 26.404$ (7) Å, $\alpha = 79.82$ (2)°, $\beta = 82.00$ (2)°, $\gamma = 85.51$ (2)°, and $Z = 6$. This binuclear complex contains both a six-coordinate molybdenum atom with an N_3S_3 coordination sphere and a five-coordinate molybdenum atom having only sulfur donor ligands. There are five different types of molybdenum–sulfur bonds in 3.

Introduction

Recently, we have used the bulky tridentate ligand hydrotris-(3,5-dimethyl-1-pyrazolyl)borate, $HB(Me_2pz)_3^-$, to prepare an extensive series of mononuclear six-coordinate oxo- and sulfidomolybdenum complexes with *fac* stereochemistries.[2–5] The 3-methyl groups of the ligand project beyond the metal atom and severely restrict the access of other ligands to the metal atom of the $[\{HB(3,5\text{-}Me_2pz)_3\}MoE]^{n+}$ (E = O, S; n = 1, 2) fragments. With a cone angle[6] of 225°,[7] $HB(Me_2pz)_3^-$ occupies over half the coordination sphere and thereby inhibits formation of dinuclear and polynuclear complexes with short molybdenum–molybdenum distances. However, we have now isolated three novel polynuclear complexes containing the $[\{HB(3,5\text{-}Me_2pz)_3\}MoE]^{2+}$ fragment.

These complexes are produced in low yield, but their structural features include relatively unfamiliar bridging ligands for oxomolybdenum(V), namely μ-OH and μ-S_2, and an unusual linear tetranuclear complex.[8]

Experimental Section

Materials and Methods. Potassium hydrotris(3,5-dimethyl-1-pyrazolyl)borate was prepared by literature methods.[9] All reactions were performed under an atmosphere of pure dinitrogen with use of dried and deoxygenated solvents. Infrared spectra were recorded on a Perkin-Elmer 983 spectrophotometer as KBr disks. ^{1}H NMR spectra were recorded on a Bruker WM250 spectrometer with chemical shifts referenced to internal TMS.

Preparation of Compounds. $[\{HB(Me_2pz)_3\}MoS(\mu\text{-}S)_2MoO(\mu\text{-}OH)]_2$ (1). This compound was isolated as a byproduct of the preparation of $[\{HB(Me_2pz)_3\}Mo(CO)_2]_2S$.[10] During the final step in the synthesis, chromatography on silica gel with dichloromethane as the eluant, the main product $[\{HB(Me_2pz)_3\}Mo(CO)_2]_2S$ eluted as a green fraction, followed by yellow and then red fractions. Partial evaporation of the red fraction and addition of dry ether gave red-brown microcrystals of the product (25 mg) as the ether solvate. Anal. Calcd for $C_{38}H_{64}B_2Mo_4N_{12}O_6S_6$: C, 33.00; H, 4.67; N, 12.16. Found: C, 32.19;

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