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Registry No. 1, 92842-97-2; 2, 92842-98-3; 3, 92998-18-0; 4, 92998-19-1; 5, 92763-30-9; [(diphos)Rh(acet)₂]BF₄, 92763-31-0; *mer,trans*-IrHCl₂(PMe₂Ph)₃, 12099-72-8; *mer,trans*-IrHCl₂(PEt₂Ph)₃, 19414-05-2; *mer,trans*-IrHCl₂(PEt₃)₃, 19414-03-0; *mer,cis*-IrH₂Cl(PEt₃)₃, 92842-99-4; *mer,cis*-IrHCl₂(PMePh₂)₃, 22829-32-9; [(di-

phos)Rh(CO)₃]BF₄, 92763-33-2; [(diphos)Rh(CH₃CN)₂]BF₄, 92763-35-4.

Supplementary Material Available: Tables containing calculated hydrogen positions for compounds 3 and 4 (Tables A and D), thermal factors (Tables B and E), observed and calculated structure factors (Tables C and F), and bond lengths and angles involving P-C and B-F bonds (Table G) (96 pages). Ordering information is given on any current masthead page.

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Preparation and Structure of a New Kind of an Extended Partially Oxidized Linear-Chain Compound: *catena*-(μ -Bromo)bis((1*R*,2*R*)-cyclohexanediamine)nickel(2.77) Bromide

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The new extended partially oxidized linear-chain nickel compound *catena*-(μ -bromo)bis((1*R*,2*R*)-cyclohexanediamine)-nickel(2.77) bromide, [Ni(chxn)₂Br]Br_{1.77}, has been prepared and characterized by its spectral and magnetic properties. The crystal structure has been determined by single-crystal X-ray analysis using three-dimensional diffractometer data. The compound crystallizes in the orthorhombic space group *I*222 with two formula units in the unit cell. The lattice parameters are $a = 23.544$ (3) Å, $b = 7.095$ (2) Å, and $c = 5.232$ (6) Å. The structure contains chains of Ni(chxn)₂ units connected by bromide ions with the Ni-Br distances along the chain = $c/2 = 2.626$ Å. An 11.5% deficiency in the occupation of the bromide counterionic site has been observed, leaving the nickel atoms with an average oxidation state of 2.77. The electronic structure is discussed in the light of the structural, spectral, and magnetic properties.

Introduction

Mixed-valence linear-chain halogenated platinum and palladium amines have received much attention during the last decade, as described in a recent review by Keller.¹

It has been claimed that nickel forms similar salts; however, there is some confusion about the nature of the halogen-oxidized bis(diamine)nickel complexes. Some have been classified as "tervalent nickel complexes",² whereas others have been classified as Ni(II)-Ni(IV) mixed-valence complexes.³ With some macrocyclic tetraamine ligands, monomeric trivalent nickel complexes are indeed formed.⁴

All reported halogen-oxidized aliphatic nickel complexes have been formulated as stoichiometric compounds, but in the present work we show that at least the bromine-oxidized (1*R*,2*R*)-cyclohexanediamine (chxn) nickel complex is nonstoichiometric and is best described as a partially oxidized nickel(II) system. Although partially oxidized nickel complexes have been reported earlier, all of these are complexes with conjugated π -ligands (e.g. dioximes) oxidized with iodine.⁵ The ESR properties of these compounds show that they have not been oxidized at the metal site; rather, they should be classified as Ni(II) complexes with radical ligands. To our knowledge this is the first report on a single-valent nonstoichiometric extended halogen-bridged chain complex.

Experimental Section

Preparation. *catena*-(μ -Bromo)bis((1*R*,2*R*)-cyclohexanediamine)nickel(2.77) Bromide. A solution of [Ni(chxn)₂]Br₂ in 2-methoxyethanol was prepared by refluxing a mixture of [Ni(chxn)₃]Br₂⁶ (0.64 g, 1 mmol) and anhydrous nickel (II) bromide

Table I. Crystal Data

orthorhombic <i>I</i> 222	$T = \text{room temp}$
$a = 23.544$ (3) Å	$Z = 2$
$b = 7.095$ (2) Å	mol wt ^a = 508.4
$c = 5.232$ (6) Å	$\rho(\text{obsd}) = 1.95 \text{ g cm}^{-3}$
$\mu(\text{Mo K}\alpha) = 74.54 \text{ cm}^{-1}$	$\rho(\text{calcd}) = 1.93 \text{ g cm}^{-3}$
$V = 874.03 \text{ \AA}^3$	

^a Molecular weight refers to the asymmetric unit [Ni(C₆H₁₂N₂)₂Br]Br_{1.77}.

(0.109 g, 0.5 mmol) for 1 h. The resulting gray solution was placed in a beaker in the diffusion cell. In the bottom of the cell was placed a solution of bromine (0.1 g, 1.25 mmol) in tetrachloromethane (1 mL). Upon this solution was carefully placed a 4-cm layer of dioxane. The cell was closed and kept in the dark for 3 days, during which time dark brown crystals up to 1 mm in size were formed. Anal. Calcd for C₁₂H₂₄N₄Br_{2.77}Ni: C, 28.35; H, 5.55; N, 11.02; Br, 43.54; Ni, 11.55. Found: C, 27.90; H, 5.65; N, 10.95; Br, 42.35; Ni, 12.30.

Instrumental Details. The polarized reflectance spectra were recorded on a wide-band reflectometer with a Perkin-Elmer 98 quartz prism monochromator.

Magnetic susceptibility was measured by the Faraday method using Hg[Co(SCN)₄] as a standard. The equipment has been described elsewhere.⁷

Raman spectra were obtained from a powder in a pressed KBr plate by using a Jarrell-Ash 25-101 double monochromator. Exciting radiation was provided by a Sp 165-01 krypton laser and a CR argon laser.

The single-crystal X-ray diffraction data were collected from a crystal with the dimensions 0.04 × 0.28 × 0.25 mm by using an Enraf-Nonius CAD4F diffractometer with graphite monochromatized Mo K α radiation ($\lambda = 0.71073$ Å).

Crystal Data and Intensity Measurements. Unit cell dimensions were obtained from setting angles for 10 reflections.

The results from the least-squares refinement of the cell constants are $a = 23.544$ (3) Å, $b = 7.095$ (2) Å, and $c = 5.232$ (6) Å. The systematic absences indicated four possible space groups: *I*222, *I*2₁2₁, *Im*m2, and *Im*mm. The cell dimensions of the related compound [Pt(C₆H₁₄N₂)₂Br]₂ are $a = 23.80$ (2) Å, $b = 7.009$ (6) Å, and c

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Table II. Fractional Atomic Coordinates and Equivalent Isotropic Thermal Parameters^a

	x	y	z	$B_{\text{eq}}, \text{\AA}^2$
Ni	0.0000	0.0000	0.0000	1.7 (5)
Br1	0.0000	0.0000	0.5000	2.7 (5)
Br2	0.5857 (3)	0.000	0.0000	3.4 (5)
N1	0.0597 (12)	0.1895 (42)	0.0080 (191)	2 (2)
C1	0.1145 (17)	0.0929 (65)	0.0678 (79)	2 (3)
C2	0.1666 (17)	0.2081 (63)	0.0254 (198)	3 (4)
C3	0.2199 (20)	0.0903 (80)	0.0745 (121)	4 (4)

^a Estimated standard deviations refer to the last digit(s).

= 5.373 (4) Å. Cell dimensions and the powder diagram of the title compound compare well with those of the platinum complex. We therefore concluded that the compounds must be isomorphous and accordingly belong to the same space group $I222$ (No. 23).

The results from the elemental analysis indicated a deficiency of bromide compared to the stoichiometric formula $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2\text{Br}]_{1.77}\text{Br}_2$. Cell contents of two units of $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2\text{Br}]_{1.77}\text{Br}_2$ gives a calculated density of 1.93 g cm⁻³. The measured density determined by flotation in a mixture of CH_2ClBr and CHBr_3 is 1.95 g cm⁻³. The linear absorption coefficient (Mo $K\alpha$) has a value of 74.54 cm⁻¹. The crystal data are summarized in Table I.

Reflections hkl and $\bar{h}\bar{k}\bar{l}$ in the range $2.0 < \theta < 25^\circ$ were measured by applying the ω -scan technique with $\Delta\omega = (1.80 + 0.35 \tan \theta)^\circ$. The relatively large scan angle was used because of the width of the reflections probably caused by an excessive mosaic structure. Systematically absent reflections ($h + k + l = 2n + 1$) were not measured. Symmetry-equivalent reflections were averaged to produce a unique set of 767 reflections, of which 167 having $F^2 < 2.5\sigma(F^2)$ were designated "not observed". The reflections were measured with a horizontal variable detector aperture width of $(4.00 + 2.00 \tan \theta)$ mm. The vertical size of the detector slit was fixed to 4.00 mm. A prescan determined the speed of the final scan so that $\sigma(I)/I < 0.04$. At the beginning and the end of a scan, one-sixth of the scan time was used for background measurements. Three reflections, (12,0,0), (060), and (002), were used for orientation control every 100 reflections. The intensity of (104) was checked every 3 h. Lorentz, polarization, and absorption corrections were applied, but no extinction correction was made.

Structure Solution and Refinement. Ni and Br positional parameters were deduced from the Patterson map and the isomorphism with $[\text{Pt}(\text{chxn})_2\text{Cl}]_2\text{Cl}_2$. A Fourier synthesis with phases from the Ni and Br positions revealed all the non-hydrogen atoms. The positional H parameters were calculated and included in the last cycles of refinement but were not allowed to vary. In the full-matrix minimization of $\sum w(|F_o| - |F_c|)^2$ the weighting function was $w = 1.0/[1 + (F_o - b)/a]^2$ with $a = 25.0$ and $b = 10.0$, as this choice gave an acceptable weight analysis. Anisotropic thermal parameters were used for all non-hydrogen atoms. An independent refinement of population parameters p for the two different bromine positions $c(0, 0, 1/2)$ and $e(x, 0, 0)$ confirmed the previously mentioned deficiency in bromine with the results $p_c = 0.995$ (30) and $p_e = 0.887$ (23). The difference $p_c - p_e = 0.108$ is 2.84 times the standard deviation of the difference $(0.030^2 + 0.023^2)^{1/2}$, an indication of a population parameter p_c significantly smaller than 1. The values of p_c and p_e correspond to the formula $[\text{Ni}(\text{C}_6\text{H}_{14}\text{N}_2)_2\text{Br}]_{1.77}$.

The final agreement index, $R = \sum ||F_o| - |F_c|| / \sum |F_o|$, was 0.076. All calculations were performed on a Univac 1110 computer by using the X-RAY 76 system.⁸ The atomic scattering factors for Ni(III) and the neutral atoms C, H, and N were taken from ref 9. Tables of observed and calculated structure factors are available as supplementary material. The final positional and thermal parameters are given in Table II. Interatomic bond lengths and angles are quoted in Table III.

Results

Preparation of the Complex. An essential problem in characterization of the halogenated nickel amine complexes

Table III. Bond Distances and Angles^a

bond dist, Å		bond angle, deg	
Ni-N1	1.95 (3)	N1-Ni-N1'	88 (1)
N1-C1	1.49 (5)	N1-Ni-N1''	93 (1)
C1-C1'	1.45 (6)	Ni-N1-C1	139 (2)
C1-C2	1.49 (6)	N1-C1-C1'	108 (4)
C2-C3	1.53 (7)	N1-C1-C2	115 (4)
C3-C3'	1.50 (8)	C1'-C1-C2	114 (4)
		C1-C2-C3	111 (4)
		C2-C3-C3'	112 (5)

^a Estimated standard deviations in parentheses refer to the last digit(s).

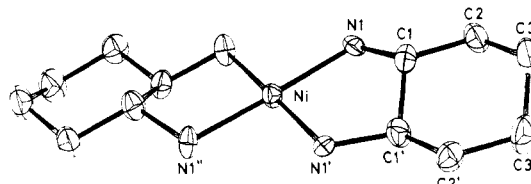


Figure 1. Perspective view of a nickel atom with surrounding ligands. The atoms are represented by thermal ellipsoids enclosing 50% probability. The atom-numbering scheme is quoted.

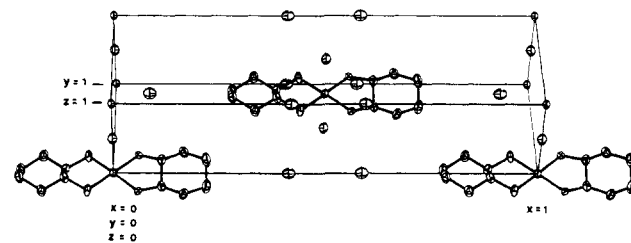


Figure 2. Perspective view of the unit cell showing nickel with coordinating ligands and the spatial arrangement of bromide ions.

seems to be the great variety of substances that can be obtained by negligible modifications of the preparation procedure. Thus, it has been suggested that a fast chlorine bubbling of a solution of $[\text{Ni}(\text{en})_2]^{2+}$ in ethanol leads to a Ni(III) species, whereas slow Cl_2 and N_2 bubbling gives the mixed-valent Ni(II)-Ni(IV) species.¹⁰

In our preparation we have chosen (1*R*,2*R*)-cyclohexanediamine (chxn) as the ligand, mainly because this diamine with platinum forms the Wolfram red salt type halogen-bridged linear-chain complex with the shortest Pt-Pt distance yet reported.¹¹

In order to get a well-characterized salt, it proved necessary to find a way of growing fairly large crystals of the material. The oxidized phase can only be grown from nonaqueous solution, and because of the strong oxidizing power of bromine, most of the usual solvents could not be used. However, we found 2-methoxyethanol to be stable enough in a preparation running for a few days. In the preparation we used a slow liquid to gas to liquid diffusion of bromine in a thermostated cell. The bromine gas slowly diffused from a dioxane solution into a solution of bis((1*R*,2*R*)-cyclohexanediamine)nickel(II) bromide in dry 2-methoxyethanol. Crystals, up to 1 mm in size, of the title compound were formed during 3 days.

Whereas all reported halogen-oxidized nickel amine complexes have been formulated as stoichiometric nickel amine complexes with a nickel to halogen ratio of 3,^{2,3,10} the chemical analysis of the title compound shows a deficiency in the bromide content of 7.7%, corresponding to a Br to $\text{Ni}(\text{chxn})_2$ ratio of 2.77.

The crystals are black and shiny. Thin crystals are transparent and exhibit a striking pleochroism, being black when

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the electric vector is vibrating along the needle axis and red-brown in the perpendicular direction.

Description of the Structure. From a crystallographic point of view the title compound is isomorphous with the mixed-valence compound $[\text{Pt}(\text{chxn})_2\text{Cl}]\text{Cl}_2$,¹¹ however, as we shall show, they are quite different chemically.

The structure is interpreted in terms of chains of planar $\text{Ni}(\text{chxn})_2$ units (Figure 1) connected by bromide ions with the Ni-Br bonds parallel to the *c* axis (Figure 2). An oscillation photograph around the *c* axis at room temperature has no indication of diffuse spots or lines between the layer lines; thus, no evidence for a superstructure along *c* occurs. The immediate conclusion of course is that the compound actually is single valent, but this argument is invalidated by the fact that the diffraction pattern from the mixed-valence complex $[\text{Pt}(\text{chxn})_2\text{Cl}]\text{Cl}_2$ is similar in showing no diffuse spots or lines between the layer lines. In the latter case the system has been classified as a three-dimensional disordered structure.¹ The Patterson function along the *w* coordinate around the point $(u, v, w) = (0, 0, 0.5)$ has been analyzed. The X-ray resolution power is $\lambda/2 - 0.36 \text{ \AA}$. Accordingly, a *z*-coordinate displacement from the bridging-bromine position $(x, y, z) = (0, 0, 0.5)$ of more than 0.18 \AA should cause a detectable splitting of the Patterson top at $(u, v, w) = (0, 0, 0.5)$. This is not observed. Thus, in the structure of the nickel complex there is no indication of a splitting of the electron density from the bridging bromide. This result, however, does not necessarily exclude a mixed-valence structure. In the case of $[\text{Pt}((\pm)\text{-pn})_2\text{Br}]\text{Br}_2$ ($(\pm)\text{-pn} = \text{racemic } 1,2\text{-propylenediamine}$) a structure with a centrally placed bromide has been reported,¹² despite the fact that the resonance Raman spectrum¹³ (see below) clearly shows that the compound is a mixed-valence system. This is an exception from the normal pattern, where the calculated electron density from the bridging halogen is divided equally between two sites as has been observed for $[\text{Pt}(\text{chxn})_2\text{Cl}]\text{Cl}_2$.

A most important aspect of the structure is the observed bromide ion deficiency. Independently of the analytical data, the refinement of the population parameters gave the same Br to $[\text{Ni}(\text{chxn})_2]$ ratio of 2.77. It is remarkable that the bromide deficiency is found exclusively among the counterionic sites to the chain, so that the nickel-bromide spine of the structure is intact.

The Ni-Br distance along the chain is half the crystallographic *c* axis, 2.626 \AA , which is surprisingly close to half the *c* axis of $[\text{Pt}(\text{chxn})_2\text{Br}]\text{Br}_2$ (2.686 \AA) and the reported Pt-Br distance in $[\text{Pt}((\pm)\text{-pn})_2\text{Br}]\text{Br}_2$ (2.673 \AA). For the Ni case the distance is about 0.1 \AA larger than expected from the ionic radii of low-spin Ni(III) and Br^- (2.52 \AA) but fairly close to what has been seen for high-spin Ni(II) and Br^- (2.674 \AA).¹⁴ On the other hand, the distance from Ni to the amine nitrogens of $1.95 (\pm 0.03) \text{ \AA}$, is considerably shorter than the average high-spin Ni(II)-amine distances of $2.10\text{--}2.13 \text{ \AA}$,^{14,15} but the value is rather close to typical Ni-N distances in low-spin square-planar tetraamine-nickel(II) complexes (1.95 \AA).¹⁶ The N-Ni-N angle in the five-membered chelate ring, 88.1° , is significantly larger than the corresponding N-Pt-N angle ($83.7 \pm 0.2^\circ$) in the isomorphous Pt salt,¹¹ which seems to reflect the differences in the metal to ligand distances, as the N-N distances stay the same (2.71 \AA). Angles and distances in the *trans*-1,2-cyclohexanediamine, Table III, are within two standard deviations of those found in other *trans*-1,2-cyclo-

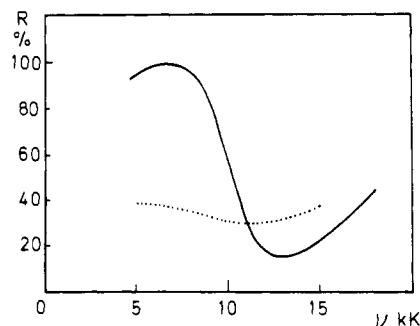


Figure 3. Single-crystal specular reflectance spectrum of $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_{1.77}$ with the electric vector along the *c* axis (—) and with the electric vector perpendicular to the *c* axis (...) (298 K).

hexanediamine complexes.¹¹ The estimated standard deviations of the cyclohexanediamine atoms are rather large, probably caused by the ligand coordination to Ni in different oxidation states.

In contrast to the Wolfram red salt, the *trans*-1,2-cyclohexanediamine complexes are anhydrous, so if hydrogen bonds are crucial in knitting the structure together, only hydrogen bonds between the ionic bromide and the amino groups can contribute to this kind of stabilization. These distances are 3.44 \AA , which is typical for what is seen in ammonium bromides.¹⁷ It is normally assumed that hydrogen bonds are responsible for the communication between the chains and development of three-dimensional order. However, Coulombic interactions might also be of importance in this respect. All the bromide ions are located very close to each other in bands along the line $(x = 0, z = 0.5)$. The smallest Br-Br distances in the band are close to 4.0 \AA , so one should expect rather large Coulombic interactions to develop along this Br⁻ net. An interaction of this kind could give the whole structure some two-dimensional character. There actually seems to be a correlation between the *b* and *c* axes among the published structures in such a way that a shortening of the *c* axis corresponds to a shortening of the *b* axis.

The fact that about every fourth of the counterionic bromides are missing should of course have some influence on the positions of the other ions, so the nonstoichiometry might be the origin of the rather large thermal parameters observed for these bromides. In $[\text{Pt}((\pm)\text{-pn})_2\text{Br}]\text{Br}_2$ the distance between the counterionic and the bridge bromides is as low as 3.89 \AA , due to a slight deviation from linearity of the Pt-Br spine.¹² It is tempting to suggest that this compound too is nonstoichiometric.

Electronic Spectra. The single-crystal specular reflectance spectrum of $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_{1.77}$ is shown in Figure 3. The spectrum is quite different from what has been reported for other similar compounds,^{2,10,23} but as usual it is strongly polarized along the *c* axis. The main reflectance in the near-infrared spectrum, which normally is assigned to arise from an intervalence-transfer band, is in this case strongly red-shifted, and we suggest that it corresponds to the electronic band gap of an extended system.

Resonance Raman Spectra. The resonance Raman technique has been shown to be an efficient tool in assigning the mixed-valence structure to halogen-bridged systems, because irradiation within the intervalence ($\text{M}^{\text{IV}}\text{-M}^{\text{II}}$) band contour leads to a strong intensification of the Raman band attributed to the totally symmetric stretching mode $\nu_{\text{sym}}(\text{X-M}^{\text{IV}}\text{-X})$.^{13,23} In the case of $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_{1.77}$ the Raman spectra were very difficult to record due to the very effective absorption for most available laser frequencies. At 514.5 nm , however, we obtained a weak broad signal centered at 190 cm^{-1} and two

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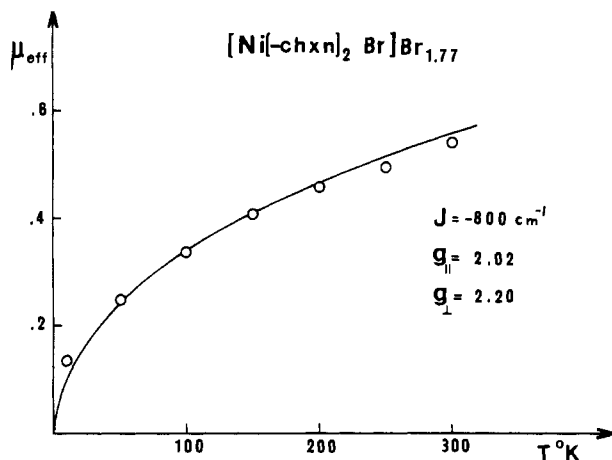


Figure 4. Magnetic moment of the title compound as a function of temperature. Solid curve: the Ising equation with the parameters indicated.

narrow signals at 77 and 67 cm^{-1} .

A factor-group analysis based on the chain of Ni and Br, having the site symmetry D_2 , tells us that no symmetric vibrations are Raman allowed in the Ni-Br chain chromophore, so a resonance-enhanced Raman spectrum as seen for a Wolfram red salt system is not expected. On the other hand, three non totally symmetric modes are Raman allowed, so one of these might be the signal at 190 cm^{-1} . Totally symmetric lattice modes are expected from the vibration of the counterionic bromides. The lines at 77 and 67 cm^{-1} we assign to this type of vibration.

Magnetism. The paramagnetic susceptibility of $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_{1.77}$ was measured by the Faraday method in the range 5–295 K, giving the results in Figure 4 (after correcting for the diamagnetism with Pascal constants). The small temperature variation of the magnetic moment might indicate that the paramagnetism is due to a Pauli paramagnetism of a conductor. However, we also have tried to fit the data to an exchange-coupling model of an extended chain of $S = 1/2$ spin (low-spin Ni(III)), the Ising model, for which a closed solution is known.¹⁸ The fit is reasonably good, Figure 4, but the coupling constant $J = -800 \text{ cm}^{-1}$ seems to be unreasonably large, considering the fairly large Ni-Br distance. The moment is not approaching zero for $T \rightarrow 0$, as demanded in the Ising model; however, if the effect of substituting low-spin Ni(II) ($S = 0$) into the chain is considered, the extended system will be replaced by a system of segments. For such a discrete antiferromagnet the moment at $T = 0$ is either finite or zero depending on the nuclearity being either odd or even.

Discussion

In the following we shall discuss which energetic and structural effects are responsible for the choice of either a mixed-valence system or a single-valence system as the ground state.

It is well-known that the Born-Haber-cycle calculations describe the energetics in the formation of an ionic lattice quite well. Assuming that the one-dimensional lattice energy of the M-X chain can be estimated from the Kapustinskii formula and using the relevant ionic radii, we see that only for the platinum case is the fourth ionization energy small enough to stabilize the M(II)-M(IV) lattice over the M(III) lattice. The difference between chloride and bromide as X is without significance. Especially in the nickel case is the destabilization of the mixed-valence situation very large (on the order of 200

kJ/mol). However, the mixed-valence situation might be stabilized by the extra ligand field stabilization gained by going from the M(III) to the M(IV) site. This effect can explain why the palladium chain compounds are mixed-valence systems but the energy contribution is far from sufficient to make a nickel chain compound mixed valent.

In this discussion we have neglected any stabilizing effects from extended band structure formation. Recent band structure calculations on $[\text{Pt}(\text{NH}_3)_4\text{X}]^{2+}$ chains¹⁹ suggested that in the X = Br case the mixed-valence structure is stabilized by 96 kJ/mol compared to the single-valence situation. Due to the larger extension of the Pt d_{z^2} orbitals, this figure must be considered as an upper limit for the stabilizations expected for other systems. So, even with the combined effects of ligand field stabilization and band structure formation, the nickel systems may still be single valent.

The difference between the mixed-valence and the single-valence structures can in some cases be very small. Thus in CsAuCl_3 a transition from a mixed-valence structure to a single-valence structure has been observed at high pressure.²⁰

The structural, magnetic, and optical properties of $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_{1.77}$ all indicate that the system has an extended band structure and then should be considered to be an example of a one-dimensional class III system in the Robin and Day classification.²² Interactions between the $[\text{Ni}(\text{chxn})_2\text{Br}]$ units occur primarily through the metal-halide-metal bridge along the chain, and hence only the d_{z^2} band has appreciable bandwidth; however, it will probably not exceed 8000 cm^{-1} as bandwidth calculations on $[\text{Pt}(\text{NH}_3)_4\text{Cl}]^{2+}$ are of this order of magnitude.¹⁹ According to the stoichiometry, this d_{z^2} band should be a 0.62-filled band. It is a well-established fact that one-dimensional band structures are inherently unstable with respect to distortions along the stacking axis (Peierls distortion). Such distortions open a gap in the band. A quantitative calculation of the energy variation in this process as a function of the distance from the midpoint between the metal ions to the bridging halogen(s) has been performed by Whangbo for $[\text{Pt}(\text{NH}_3)_4\text{X}]^{2+}$ (X = Cl, Br) chains.¹⁹ The limitations in the resolution due to the wavelength of the X-ray source ($\lambda = 0.71 \text{ \AA}$) indicate an upper limit of 0.18 \AA for the distance d , in the case of $[\text{Ni}(\text{chxn})_2\text{Br}]\text{Br}_{1.77}$ at room temperature. This puts the gap below 10 000 cm^{-1} , in accordance with the specular reflectance spectrum shown in Figure 3.

If the system is distorted in its group state, a 4c or a 8c superstructure is expected to be found in the diffuse X-ray pattern. The first case corresponds to a 1:3 Ni(II):Ni(III) formulation, whereas the other case corresponds to a 5:3 Ni(II):Ni(IV) formulation.

The exceptionally intense electronic absorption of the title compound might be understood if it is considered to be a type III mixed-valence compound, where a considerable electronic delocalization between the Ni(II) and Ni(III) ions occurs through the bridging halide. In that case the metal to metal charge-transfer transitions acquire a high transition probability and therefore become very intense. The fact that the title compound does not give a resonance-enhanced Raman spectrum with an overtone progression supports the conclusion that this material is single-valent partially oxidized Ni(II). This statement, however, does not seem to be general for halogenated amine-nickel(II) systems. In the case of $[\text{Ni}(\text{en})_2\text{Cl}]\text{Cl}_2$, a progression in an intense line at 263 cm^{-1} suggests that at least this compound can be formulated as a

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mixed-valence of Ni(II)-Ni(IV) system.³ However again, the corresponding bromide salt did not give a resonance Raman spectrum.

In a future paper we will describe the conductivity properties of this material.

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Supplementary Material Available: A listing of observed and calculated structure factors, Figure 5, showing a graph of the Patterson function along the *w* coordinate around the point (*u*, *v*, *w*) = (0, 0, 0.5), and lists of anisotropic thermal parameters, *R* factors, and bond distances and angles (15 pages). Ordering information is given on any current masthead page.

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Reactions of Tetrathiometalates, MS₄²⁻ (M = Mo, W). Syntheses and Properties of M₂S₄²⁺-Containing Compounds. Structure of Bis(tetraphenylphosphonium) Bis(μ-sulfido)bis(sulfido(1,2-ethanedithiolato)tungstate(V)), [P(C₆H₅)₄]₂[W₂S₄(S₂C₂H₄)₂]

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Heating ammonium salts of MS₄²⁻ (M = Mo, W) in DMF for 1-3 h in the presence of either 1,2-ethanedithiol or *o*-aminobenzenethiol (LH₂) provides a convenient route to M₂S₄L₂²⁻ compounds. The W and Mo compounds have similar spectroscopic and structural properties. The complex [P(C₆H₅)₄]₂[W₂S₄(1,2-ethanedithiolato)₂] crystallizes in the monoclinic crystal system, space group *P*2₁/*n*, with unit cell dimensions *a* = 16.126 (7) Å, *b* = 25.03 (1) Å, *c* = 13.021 (6) Å, and β = 101.73 (4)° and a unit cell volume of 5145 (4) Å³. The dinuclear complex contains a *syn*-W₂S₄²⁺ core. The W-W distance of 2.86 Å is identical with that in the Mo analogue but is 0.05 Å shorter than the corresponding distance in W₂S₄(WS₄)₂²⁻. It is possible that internal redox is involved in the formation of M₂S₄²⁺ cores.

The binary tetrathiometalate anions, MS₄²⁻ (M = Mo, W), have been known for almost 100 years.¹ Until recently, studies on these anions were carried out mainly in aqueous solvents at ambient temperatures.^{1,2} In nonaqueous solvents and at moderately elevated temperatures MS₄²⁻ undergoes interesting thermal reactions.³ Studies of these reactions may lead to insight regarding the mechanism of thermal conversion of MS₄²⁻ to MS₃ and ultimately to MS₂.⁴ In *N,N*-dimethylformamide, at 90 °C, (NH₄)₂MoS₄ gives the stable molecular ion Mo₃S₉²⁻ (i.e., (MoS₃)₃²⁻),³ which may be an intermediate in the formation of MoS₃ from MoS₄²⁻.

The formation of M₃S₉²⁻ from MS₄²⁻ probably involves an internal redox reaction where coordinated S²⁻ is the reducing agent. However, in the presence of external reducing agents such as 1,2-ethanedithiol (edtH₂) or *o*-aminobenzenethiol (abtH₂), a product containing the M₂S₄²⁺ core is obtained. This reaction is of considerable synthetic interest. Previously, Mo₂S₄²⁺ compounds had been prepared in high yield starting from Mo₂(S₂)₆²⁻.⁵ However, the tungsten analogue, W₂(S₂)₆²⁻, has not been prepared, thereby precluding the preparation of W₂S₄²⁺ species via this route. This is unfortunate since heretofore examples of compounds containing the W₂S₄²⁺ core are limited to two, namely W₄S₁₂²⁻⁶ and W₂S₄(S₂PR₂)₂.⁷ Of these two, only the structure of the tetranuclear ion, W₄S₁₂²⁻, has been confirmed.⁶

In this report, we describe a convenient route to preparing M₂S₄²⁺-containing compounds using MS₄²⁻ as the starting material. We also confirm the formation of compounds containing the W₂S₄²⁺ core by reporting the full crystal

structure determination of [P(C₆H₅)₄]₂W₂S₄(edt)₂.

Experimental Section

Syntheses. Solvents, *N,N*-dimethylformamide (DMF) and acetonitrile, were obtained from Burdick & Jackson. DMF was distilled once before use, and CH₃CN was refluxed over CaH₂ and then distilled before use. The thiols, 1,2-ethanedithiol (edtH₂) and *o*-aminobenzenethiol (abtH₂), were used as received from Aldrich Chemical Co. (NH₄)₂WS₄ and (NH₄)₂MoS₄ were prepared as previously described.³ Elemental analyses were performed by Galbraith Laboratories and the Analytical and Information Division of Exxon Research and Engineering Co.

[N(C₂H₅)₄]₂Mo₂S₄(edt)₂. A degassed solution of edtH₂ (0.63 mL, 7.5 mmol) in 32 mL of DMF was added to (NH₄)₂MoS₄ (1.26 g, 4.9 mmol) under an atmosphere of N₂. The resulting solution was stirred and heated at 90 °C for 60 min. After the solution was cooled to room temperature, [N(C₂H₅)₄]Br (1.5 g) was added and allowed to dissolve. The reaction mixture was filtered, and diethyl ether was added to the filtrate to the point of incipient precipitation. When the filtrate was allowed to stand and cool, (~-20 °C), orange-red

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