measurements were done in nitrogen atmosphere. In every case care was taken to obtain a flat current–voltage baseline over the required voltage range in the absence of the electroactive species.

For wire electrodes the diffusion process is cylindrical whereas the important equations of cyclic voltammetry[4] refer to planar electrodes (linear diffusion). It was shown by Nicholson[23] that at relatively high scan rates the observed peak positions for the two types of diffusion are the same within experimental error. We have thoroughly checked[19] that this is so in our experimental setup at and above the scan rate of 0.01 V s^{-1}.

2. Buffers. Acetate (pH 0.65–5.20), phosphate (pH 5.29–8.04), and borate (pH 7.80–10.00) buffers were prepared in the usual manner[25] in 0.1 M NaCl. The pH value of each buffer was measured experimentally just before use. The electrolytes in the buffer and the NaCl together acted as the supporting electrolyte. The measurements were made on 50.0 ml of solution.

D. Constant-Potential Coulometry. The same cell and electrode assembly as described above were used for this purpose except that the working electrode was a platinum foil of cylindrical construction (effective area ~180 cm^2). The solution was constantly stirred during electrolysis. The potential was held constant using the potentiostatic device described earlier.

E. EPR Spectra and Magnetic Moments. The powder and solution spectra were recorded on a Varian V4502 EPR spectrometer operating at the X-band microwave frequency. Magnetic moments were measured as described earlier.[1]

Registry No. Ni(Me$_2$L)$^{2+}$, 55188-33-5; Ni(H$_2$Me$_2$L)$^{2+}$, 55188-31-3; Ni(Me$_2$L)$^+$, 59980-37-9; Ni(HMe$_2$L)$^+$, 60306-03-8; Ni(Me$_2$L), 59980-38-0; Ni(RR′L)$^{2+}$ (R = Me, R′ = Et), 55758-52-6; Ni(H$_2$RR′L)$^{2+}$ (R = Me, R′ = Et), 55822-46-3; Ni(RR′L)$^+$ (R = Me, R′ = Et), 60338-53-6; Ni(RR′L) (R = Me, R′ = Et), 60306-04-9; Ni(RR′L)$^{2+}$ (R = Et, R′ = Me), 55758-50-4; Ni(H$_2$RR′L)$^{2+}$ (R = Et, R′ = Me), 55758-44-6; Ni(RR′L)$^+$ (R = Et, R′ = Me), 60306-05-0; Ni(RR′L) (R = Et, R′ = Me), 60306-06-1; Ni(RR′L)$^{2+}$ (R = Me, R′ = Ph), 55758-54-8; Ni(H$_2$RR′L)$^{2+}$ (R = Me, R′ = Ph), 55758-46-8; Ni(RR′L)$^+$ (R = Me, R′ = Ph), 60306-07-2; Ni(RR′L) (R = Me, R′ = Ph), 60306-08-3; Ni(RR′L)$^{2+}$ (R = Ph, R′ = Me), 55822-44-1; Ni(H$_2$RR′L)$^{2+}$ (R = Ph, R′ = Me), 55758-48-0; Ni-(RR′L)$^+$ (R = Ph, R′ = Me), 60306-09-4; Ni(RR′L) (R = Ph, R′ = Me), 60306-10-7; Fe(Me$_2$L)$^+$, 60325-45-3; Fe(H$_2$Me$_2$L)$^{2+}$, 60306-11-8; Fe(HMe$_2$L)$^+$, 60306-12-9; Fe(Me$_2$L), 60306-13-0.

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Spectral and Magnetic Properties of Copper(II) 1,5-Naphthyridine 1,5-Dioxide Complexes

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The di-*N*-oxide of 1,5-naphthyridine has been prepared and coordination compounds with copper(II) chloride, bromide, and nitrate have been prepared. Infrared, electronic, and electron paramagnetic resonance spectroscopies have been used to determine the binding properties of the ligand and anions. Magnetic susceptibilities support antiferromagnetic exchange through the extended π system of the heterocyclic ligand. The magnetic data can be fit to the isotropic Heisenberg model for linear chains with $S = 1/2$ coupled magnetic ions with $J \approx -3.5$ cm^{-1} in all three complexes.

Introduction

Extended π pathways have recently been shown to propagate spin coupling of magnetic ions over long distances.[2–6] The pyrazine-bridged copper(II) nitrate[2,3,6] and the 1,5-naphthyridine-bridged copper(II) nitrate[4] complexes have measurable spin exchange even though the magnetic centers are separated in the linear chains by 6.7 and ~9 Å, respectively. In fact, the naphthyridine complex exhibits a

greater spin coupling than does the pyrazine complex. Interchain coupling may be suspected of contributing to the interactions but it has been conclusively shown[6] that no such mechanism operates significantly in the pyrazine linear-chain complex.

In this present work extension of the π system has been accomplished by preparing the di-*N*-oxide of 1,5-naphthyridine (NDO), I, and complexing it with copper(II) chloride,

Table I. Analytical Data

			% calcd			% found		
Compd	Color	Dec pt, °C	C	H	N	C	H	N
Cu(NDO)Cl$_2$	Olive	282–287	32.52	2.05	9.39	32.40	2.04	9.45
Cu(NDO)Br$_2$	Purple	279	25.33	1.45	7.19	24.93	1.57	7.27
Cu(NDO)(NO$_3$)$_2$	Olive	270	27.92	1.89	16.10	27.48	1.73	16.02
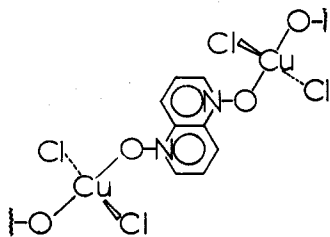
Figure 1. Postulated structure of Cu(NDO)Cl$_2$.

I
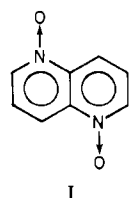
bromide, and nitrate to form complexes of the type Cu-(NDO)X$_2$. The postulated structure for the complexes is shown in Figure 1. A σ pathway for exchange is expected to be severely attenuated over such distances. Also, if interchain interactions are significant in the complexes, anion effects should be a major perturbing factor in the magnetic exchange. Due to the large size of the NDO heterocyclic ligand, anion bridging between chains should be minimal. The results of our structural and magnetic studies of the 1,5-naphthyridine 1,5-dioxide complexes are reported here.

Experimental Section

1,5-Naphthyridine 1,5-dioxide (NDO) was prepared as previously described[7] and recrystallized twice from ethanol to give fine yellow needles, mp 300–301 °C. All other chemicals were of the best available reagent or spectroscopic grades. C, H, and N analyses were performed by Schwarzkopf Microanalytical Laboratory, Woodside, N.Y., and Chemalytics, Inc., Tempe, Ariz.

Preparation of Complexes. 1,5-Naphthyridine 1,5-dioxide (0.081 g, 0.5 mmol) was dissolved in 60–75 ml of boiling absolute ethanol. The hot solution was filtered using a heated funnel and a collection flask. A solution of the appropriate copper(II) salt (1.0 mmol) dissolved in the minimum amount of absolute alcohol was added to the hot ethanolic di-*N*-oxide solution. The chloride and bromide compounds precipitated immediately whereas the nitrate complex took about 5 min for precipitation to begin. The mixtures were allowed to stand overnight at room temperature. The compounds were isolated by filtration and dried in a desiccator over phosphorus pentoxide. Analytical results are reported in Table I.

Infrared spectra (4000–200 cm^{-1}) were measured with a Perkin-Elmer 621 recording spectrophotometer using Nujol mulls on cesium iodide plates. Mull (transmission) electronic spectra were obtained with a Cary Model 14 recording spectrophotometer using a method described previously.[8] Electron spin resonance (EPR) spectra were recorded on Varian E-3 and EM-500 X-band and Magnion MVR-12X X-band spectrometers with accessories described previously.[9] The EPR spectra of the complexes were simulated using computer programs described by Venable[10] and Chasteen.[11]

Magnetic susceptibilities were determined with a Foner vibrating-sample magnetometer[12] operating at a field strength of 10 kG. Calibration of the magnetometer was checked using two standards: HgCo(NCS)$_4$[13] and (NH$_4$)$_2$Mn(SO$_4$)$_2$·6H$_2$O.[14] The more recent correction to the Weiss constant for HgCo(NCS)$_4$ was applied and both standards agreed within 2% (previously determined[15] to be the upper limit of the uncertainty in our measurements). Temperatures

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

Complex	ν-(N→O)	δ-(N→O)	γ-(C–H)	ν-(M–O)	ν-(M–X)
Cu(NDO)Cl$_2$	1205	813	795	440	315
Cu(NDO)Br$_2$	1205		793		
Cu(NDO)(NO$_3$)$_2$	1200	810	792	430	280
(NDO)	1248		786		

[a] All values ±1.0 cm^{-1}.

Table III. Electronic Spectral Data (1000 cm^{-1})

Complex	d–d	Shoulders	$\pi \to \tau^*$	$\pi \to \pi^*$
Cu(NDO)Cl$_2$	12.4	(21.2) (23.5)	27.0	41.2
Cu(NDO)Br$_2$	12.8	(20.6) (22.5)	27.3	41.2
Cu(NDO)(NO$_3$)$_2$	13.5	(22.7) (24.5)	26.9	41.2
(NDO)		23.9 (n → π^*)	27.0	41.2

were measured with a GaAs diode which had been standardized against a commercially calibrated diode.[16] A value of 60 × 10^{-6} cgsu was employed for the temperature-independent paramagnetism of the copper(II) ion and diamagnetic corrections for all the constituents were made using Pascal's constants.[17]

Results and Discussion

Infrared Spectroscopy. The infrared absorptions of interest are listed in Table II. The N–O stretching frequencies, ν(N–O), of the ligand shift to lower wavenumbers in the complexes. This is generally characteristic of coordinated pyridine *N*-oxide[18,19] but not for coordinated quinoline *N*-oxides.[20,21] The NDO ligand has structural characteristics of both. The negative shift of the ν(N–O) band reflects a diminution in the electron density in the N–O bond due to the addition of a Lewis acid, the Cu(II) ion. The ν(N–O) bands in quinoline *N*-oxides, by virtue of their slight positive shift upon coordination, are said to be coupled more strongly to the ring vibrations.[22] Also, d$_\pi$–p$_\pi$ back-bonding has been discussed as a possible cause for the positive shift.[20] The NDO ligand behaves analogously to the pyridine *N*-oxides. Our proposed linear-chain structure (Figure 1) supports this view. The kinematic coupling[23] of the adjacent ring vibrations is hindered due to the steric requirements of the linear chain. The availability of lower lying π^* orbitals for increased back-bonding in 1,5-naphthyridine vs. pyrazine (and especially lower than pyridine) has been shown to increase spin coupling between magnetic centers in the linear-chain complexes (nap)Cu(NO$_3$)$_2$[5] and (pyr)Cu(NO$_3$)$_2$.[6] Since the lowest $\pi\pi^*$ state in NDO would be expected to lie lower in energy than the corresponding band in pyridine *N*-oxide, increased back-bonding might be anticipated for the di-*N*-oxide ligand as is claimed for the quinoline *N*-oxides.[20,21] However, NDO behaves much as pyridine *N*-oxides do. Thus, it appears that the presence of two positive ions, one at each ring, has the effect of localizing the π-electron density in each ring and limiting possibilities for extensive kinematic coupling.

The absorptions for the ν(Cu–ligand) and the ν(Cu–X) bands for the nitrate and chloride complexes are listed in Table II. Resolution of bands for the bromide complex was inadequate for interpretation. The assignments in the table are consistent with previously reported values.[18,19,24–29] From the far-infrared data we can conclude that the chloride ion is nonbridging and that the nitrate ion is coordinated to the metal. Splitting of the ν(Cu–ligand) band was not observed

Table IV. Magnetic Data

	g_1	g_2	g_3	$\langle g \rangle_{EPR}$	J, cm^{-1}	$\langle g \rangle_{susc}$	$10^3 P$
Cu(NDO)Cl$_2$	2.280 ± 0.005	2.073 ± 0.005		2.142	−3.7 ± 0.3	2.10 ± 0.06	0.95
Cu(NDO)Br$_2$	2.200 ± 0.010	2.075 ± 0.005		2.117	−3.5 ± 0.3	2.10 ± 0.06	3.55
Cu(NDO)(NO$_3$)$_2$	2.244 ± 0.005	2.130 ± 0.005	2.070 ± 0.005	2.148	−3.4 ± 0.3	2.17 ± 0.06	1.30
Cu(sp)Cl$_2$[a]	2.299	2.075	2.050	2.141			
Cu(sp)Br$_2$[a]	2.27	2.071	2.042	2.128			

[a] sp = 1-sparteine. Data for pseudotetrahedral sp complexes: S. N. Choi, R. D. Bereman, and J. R. Wasson, *J. Inorg. Nucl. Chem.*, **37**, 2087 (1975).
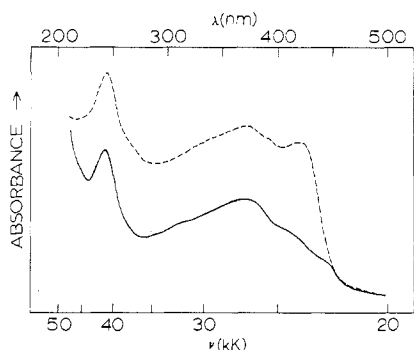

Figure 2. Electronic spectra (Nujol mulls) of NDO (- - -) and Cu(NDO)(NO$_3$)$_2$ (—).

although this has been reported for complexes in which the *N*-oxide ligand bridges two ions.[27] On the basis of frequency shifts upon complexation for the ν(N–O) ligand band, stoichiometry, and far-ir data, we suggest the structure shown in Figure 1.

Electronic Spectra. The mull (transmission) electronic spectra of NDO and Cu(NDO)(NO$_3$)$_2$ are shown in Figure 2, and data for all of the compounds are summarized in Table III. The spectra of the complexes consist of three pronounced bands in the region 11 000–45 000 cm^{-1} with the lowest energy band comprising the transitions within the manifold of d levels. Far-infrared spectral data support a four-coordinate geometry with the absence of bridging halides. Ligand size also militates against halide bridging. Magnetic data (discussed below) support the conclusions. Unfortunately, the electronic spectral data do not provide an unambiguous assignment of geometry for the halide complexes. Pyridine *N*-oxides and the chloride ion are relatively weak-field ligands[30] and square-planar and slightly to noticeably tetrahedrally distorted geometries are possible. In dimeric 1:1 CuCl$_2$–aromatic *N*-oxide complexes in which the copper(II) ion can possess a variety of environments the "d–d" transitions can be found in the range 9100–13 600 cm^{-1} depending on the substituents on the aromatic ring as well as the detailed geometry.[30] Since relatively low values of "d–d" transition energies are generally associated with low-symmetry coordination geometry and ligand–ligand repulsions are smaller in tetrahedral than in square-planar geometries,[31,32] we prefer to assign a pseudotetrahedral geometry to the Cu(NDO)X$_2$ (X = Cl, Br) compounds. The nitrate ion can coordinate in a bidentate fashion. The "d–d" band for the nitrate complex is found at higher energy than those for the halides. This could be due to the generally higher crystal field strength of oxygen donors compared to that of the halides or be due to the coordination sphere for the copper ion in the nitrate complex being distorted octahedral. Both highly distorted octahedral or distorted tetrahedral geometries are possible for the nitrate complex.

The bands at about 27 000 cm^{-1} correspond to low-lying charge transfer absorptions generally designated[33] as metal-to-ligand (d → π^*) charge-transfer bands.[34,35] However, for the NDO complexes we believe these to be internal ligand π–π^* transitions based on a comparison with the spectrum of the ligand. If the band at 27 000 cm^{-1} in the ligand spectrum
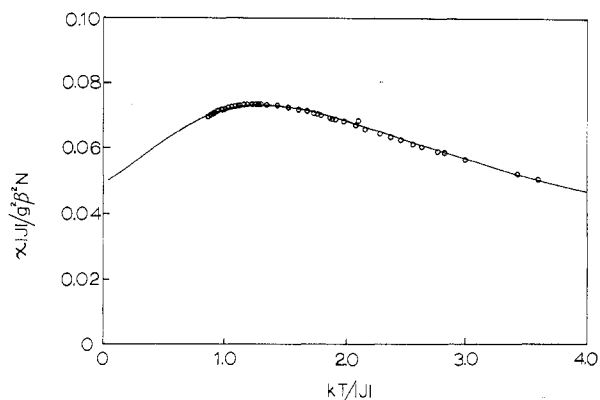

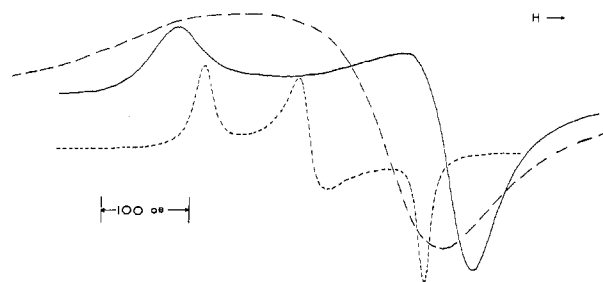**Figure 3.** Magnetic susceptibility of Cu(NDO)(NO$_3$)$_2$ as a function of temperature.

Figure 4. Room-temperature electron spin resonance spectra of polycrystalline samples of Cu(NDO)Cl$_2$ (—), Cu(NDO)Br$_2$ (- -), and Cu(NDO)(NO$_3$)$_2$ (- - -).

was due to an n → π^* transition, it would be shifted in proportion to the acid strength of the complexing metal ion.[6] No such shifts are observed. The charge-transfer bands may be contained in the two shoulders observed in all three of the complexes. However, shoulders of this nature are common in spectra of *N*-oxide complexes.[30] Although their origin is unknown, they are thought to be n → π^* bands.[34,35] It is interesting that the π–π^* bands are little affected by complexation. Generally, a red shift is observed due to the Stark effect.[38] The high-energy band at 41 200 cm^{-1} is also due to an internal ligand transition.

Magnetic Susceptibility. The magnetic behavior of *N*-oxide complexes has been extensively investigated in recent years[30,39,40] since they exhibit a wide range of magnetic properties. Magnetic characteristics of such complexes range from the virtually diamagnetic quinoline *N*-oxide complex of copper(II) chloride[40–42] to the first characterized spin-triplet ground-state dimer bis(pyridine *N*-oxide)copper(II) nitrate.[43–45] There have been a few studies[39,41] on linear-chain *N*-oxide complexes but to our knowledge this is the first detailed characterization undertaken on linear-chain di-*N*-oxide complexes. The magnetic susceptibility data as a function of temperature for Cu(NDO)(NO$_3$)$_2$ are shown in Figure 3, and the magnetic properties of all of the complexes are summarized in Table IV.

The EPR spectra of polycrystalline samples of the complexes are shown in Figure 4. The *g* values estimated from the

spectra (Table IV) are in good agreement with those obtained by fitting susceptibility data. The g values for the chloride and bromide compounds are generally supportive of the proposed structure (Figure 1) and are comparable to those of the known pseudotetrahedral l-sparteine complexes with which they are compared in Table IV. The resolution of the complete g anisotropy for the nitrate complex clearly points to the low symmetry of the coordination geometry about the metal ion. However, the EPR data for the nitrate complex do not afford more detailed structural information.

The magnetic susceptibility of an antiferromagnetically ordered linear chain of interacting spins is best treated in terms of the isotropic Heisenberg model.[46] Recent studies[3-6,47-49] have shown its applicability to copper(II) linear-chain systems. The Hamiltonian is given as

$$\mathcal{H} = -2J \sum_{i=1}^{\infty} [S_{iz}S_{(i+1)z} + \gamma(S_{ix}S_{(i+1)x} + S_{iy}S_{(i+1)y})]$$

where a negative J is indicative of antiferromagnetic interaction. The assumption of axial symmetry is implicit in the model where for γ equal to zero the anisotropic Ising model results[50] and for γ equal to 1 the isotropic Heisenberg model obtains. No explicit expression for the susceptibility of the Heisenberg model exists, but from machine calculations and subsequent extrapolations, the following approximations obtain

$$kT_{max}/|J| \simeq 1.282$$

$$|J|\chi_{max}/g^2\beta^2 A \simeq 0.073\,46$$

where the symbols have their usual meanings.[46]

The best least-squares fits, using the minimum value of

$$P = \sum_{i=1}^{n} [(\chi_i^{obsd} - \chi_i^{calcd})]^2/n$$

as the criterion for the best fit, gave the exchange values listed in Table IV. The value of P is also listed for comparison purposes. Surprisingly, the magnetic exchange in all three complexes is, for all practical purposes, the same. This observation adds support to the conclusion that all three complexes are bridged by the heterocyclic ligand in a like fashion and that exchange by way of anion bridging is negligible. Recent studies[3-6] on extended heterocyclic bridging systems have shown that magnetic exchange coupling occurs through the π system of the heterocycle. If this mechanism obtains in the case of the di-N-oxides, then the extent of exchange coupling should be reflected in the relative ordering of the orbitals involved in magnetic exchange. The electronic transitions involving the d manifold, in relation to the π and π^* orbitals of the heterocycle, should yield information as to the nature of that ordering and, ultimately, the extent of spin exchange. If exchange does occur by way of the heterocyclic bridge and this bridge should be structurally fixed in all three complexes, then anionic differences should give rise to a relatively small perturbation on the π and π^* orbitals of that bridge.

The lower the energy difference between the d manifold and the π and π^* orbitals, the greater will be the spin exchange. This can be illustrated with the following. The metal d orbitals of a magnetic couple containing the unpaired spin can be combined to give a symmetric and an antisymmetric combination of orbitals

$$d_s = 1/[2(d_A + d_B)]^{1/2}$$

$$d_a = 1/[2(d_A - d_B)]^{1/2}$$

where d_A and d_B are the metal ion orbitals containing the unpaired electron and represent a simplification to the actual form of the orbitals involved. These molecular combinations

can then form molecular orbitals with the suitable π and π^* orbitals of the ligand to give
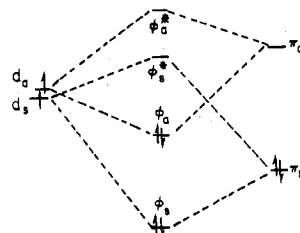
$$\phi_s = d_s + \pi$$

$$\phi_s^* = d_s - \pi$$

$$\phi_a = d_a + \pi^*$$

$$\phi_a^* = d_a - \pi^*$$

which are arranged energetically as

The singlet–triplet separation of the couple is the difference between the states Φ_S and Φ_A[51] where $\Phi_S = \phi_s^2\phi_a^2$ and $\Phi_A = \phi_s^2\phi_a^1\phi_s^{*1}$. Thus, the smaller the difference in energy between the interacting orbitals, the greater the interaction between them and the stronger the coupling of spins. In these complexes the $\pi \to \pi^*$ bands in the electronic spectra occur at approximately the same energy, and the J values, as expected, are nearly equal. The extent of the exchange coupling present is also determined by the separation between the magnetic ions. Thus, in the case of the phenazine complex of copper(II) nitrate, the exchange coupling is of a greater magnitude than that observed in the pyrazine complex,[6] those values for $|J|$ being 6.3 and 3.7 cm^{-1}, respectively, with both Cu–Cu separations being $\sim$6.7 Å. This occurs because the phenazine complex has a lower lying $\pi\pi^*$ state (27 600 cm^{-1}) than the pyrazine compound (34 600 cm^{-1}). Because the lowest $\pi\pi^*$ state in the di-N-oxide complexes lies at 27 000 cm^{-1}, comparable exchange would be presumed except for the fact that the Cu–Cu separation is much greater in the di-N-oxide. That exchange coupling of this magnitude is seen over such large separations ($\sim$12–13 Å) is remarkable; it occurs by virtue of the extensive delocalization in the π system of the ligand.

Registry No. Cu(NDO)Cl$_2$, 60184-55-6; Cu(NDO)Br$_2$, 60184-57-8; Cu(NDO)(NO$_3$)$_2$, 60184-53-4; (NDO), 27305-49-3.

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Single-Crystal X-Ray Analysis of Compounds with a Covalent Metal–Metal Bond. 5. Characterization of Halogeno-Bridged Structures of Three Dimers of Halogenobis(pentacarbonylmanganio)indium(III), [(Mn(CO)₅)₂In(μ-X)]₂ (X = Cl, Br, I)

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The oxidative insertion of In^IX into the Mn–Mn bond of $Mn_2(CO)_{10}$ in the presence of xylene led to clusters of the type $[(Mn(CO)_5)_2In(\mu-X)]_2$ (X = Cl, Br, I). All three clusters were characterized by osmometric, thermogravimetric, mass spectroscopic, ir, and Raman spectroscopic measurements. X-ray structural analysis shows that the three clusters are isomorphous and have similar molecular structures. The central molecular fragment of each cluster contains a planar centrosymmetric four-membered In_2X_2 ring. Each In atom is bonded to two μ-X atoms and to two Mn atoms in a distorted tetrahedral arrangement. The plane defined by the four Mn atoms is perpendicular to that defined by the In_2X_2 atoms. The Mn–In–Mn angles of the three clusters have the following values: X = Cl, 123.59 (3)°; X = Br, 124.97 (3)°; X = I, 126.37 (4)°. The shortest intramolecular nonbonding O···O contact lengths correspond to equatorial CO ligands of the two pairs of Mn(CO)₅ ligands above or below the In_2X_2 plane (X = Cl, 2.877 (8) Å; X = Br, 2.896 (8) Å; X = I, 2.963 (9) Å) and signify a dependence of the O···O repulsion interaction on the atomic size of the μ-X atoms. A consequence of the repulsive effect connected with the nonbonded interaction of the equatorial CO groups of the different Mn atoms is their staggered arrangement. The In_2X_2 rings have obtuse In–(μ-X)–In (X = Cl, 100.02 (5)°; X = Br, 97.42 (2)°; X = I, 94.35 (2)°) and acute (μ-X)–In–(μ-X) angles (X = Cl, 79.98 (5)°; X = Br, 82.58 (2)°; X = I, 85.65 (2)°) and the order of the nonbonded lengths In···In and X···X is In···In > X···X. These structural features of the In_2X_2 rings are reversed with respect to corresponding features of the In_2I_2 ring of the compound $[I_2In(\mu-I)]_2$ (acute In–(μ-I)–In angle, obtuse (μ-I)–In–(μ-I) angle, and the order of the length In···In < X···X), in which no comparable repulsion exists between the terminal ligands. The average In–X distances in the clusters examined are for X = Cl, 2.618 (2) Å, for X = Br, 2.757 (1) Å, and for X = I, 2.951 (1) Å. The average value of the In–Mn distance in the clusters is for X = Cl, 2.665 (1) Å, for X = Br, 2.664 (1) Å, and for X = I, 2.672 (1) Å.

Introduction

Known clusters formulated as $XIn[Mn(CO)_5]_2$ (X = Cl, Br) were isolated by the reaction of In^IBr with $Mn_2(CO)_{10}$ at 180 °C (insertion method)[1] and that of InX_3 (X = Cl, Br) with $NaMn(CO)_5$ (alkali salt method).[2] The reaction products are usually crystalline powders.[1,2] Mays[2] presumed the molecular formula $[(Mn(CO)_5)_2In(\mu-X)]_2$ (X = Cl, Br) for these solids. The present report describes the preparation of such clusters in crystalline forms (including the previously unknown one with X = I) by application of an insertion

method at a reaction temperature of 125 °C. The results of the structure determination of the clusters $[(Mn(CO)_5)_2In-(\mu-X)]_2$ (X = Cl, Br, I) by x-ray analysis and other characterizations of the clusters are given. The results of x-ray examinations with special regard to $[(Mn(CO)_5)_2In(\mu-I)]_2$ will be compared with the known structural features of $[I_2In(\mu-I)]_2$,[3] to get an impression about the influence of a bulky ligand like $Mn(CO)_5$ instead of I as the terminal ligand on the geometrical parameters of an In_2I_2 ring. This is a work to analyze those factors which determine the geometry of