range found for POTCP salts.

With regard to the azide ion we point out that the nitrogen atom positions of these partially occupied sites were clearly evident from a difference Fourier map phased using all but these atoms. The central nitrogen atom lies at $^{1}/_{2}$, 0, 0, and the terminal nitrogen atoms lie at $^{1}/_{2}$, 0, z and $^{1}/_{2}$, 0, $\bar{z}$ requiring the N_3^- group to be perfectly linear. The difference Fourier positions indicated an N–N separation of 1.16 Å, while the least-squares value converged to 1.23 (3) Å. The expected N–N separation in N_3^- is 1.16 Å[15] which is in essential agreement with our least-squares-determined value. Attempts to verify the presence of N_3^- ion using IR spectroscopy were unsuccessful, probably due to the very low concentration of azide ion in the crystal lattice.[20] We are continuing our studies of $CsCP(N_3)$ in an effort to determine if the anion content can be varied as is the case for the homologous series of MCP(FHF) complexes.[21]

Conclusions

One of the main structural findings reported here is the increased Pt–Pt separation and decreased DPO of $CsCP(N_3)$ relative to CsCP(FHF), RbCP(FHF), and CsCP(Cl). This observation is consistent with past observations[16] for these systems and with Pauling's resonating valence bond theory of metals.[17,18] A second interesting observation is that all POTCP salts that have been studied to date, which do not contain independent H_2O sites or are anhydrous, crystallize in the space group $I4/mcm$ or the nearly identical $P\bar{4}b2$. Those POTCP complexes which do contain independent H_2O sites seem most often to belong to space group $P4mm$. Another interesting point is that only POTCP complexes with "symmetrical" anions (e.g., F^-, Cl^-, Br^-, $(FHF)^-$, $(O_3SO{-}H{-}OSO_3)^{3-}$, and N_3^-)[4,6–10,22] have been prepared. As yet we have been unable to prepare salts with CN^-, OCN^-, SCN^-, or NCN^- anions. We are continuing our efforts to prepare and structurally characterize these unusual complexes and to obtain accurate temperature-dependent electrical conductivities for those salts which have already been structurally characterized.

Registry No. $Cs_2[Pt(CN)_4]\cdot H_2O$, 20449-75-6; CsN_3, 22750-57-8.

Supplementary Material Available: A listing of observed and calculated structure factors (8 pages). Ordering information is given on any current masthead page.

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(25) Note that the chemical analyses, in addition to the XDS measurements, indicate the azide content to be $(N_3^-)_{0.25}$.

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Structural and Magnetic Properties of Dimeric $[Ni_2(en)_4Cl_2]Cl_2$

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The crystal structure of dimeric $[Ni_2(en)_4Cl_2]Cl_2$ has been determined at ambient temperatures. Crystal data: space group $P2_1/c$, $Z = 2$, $a = 6.327$ (3) Å, $b = 11.311$ (2) Å, $c = 15.811$ (4) Å, $\beta = 117.81°$, $R = 2.8\%$ for 1530 reflections. The complex consists of chlorine-bridged dimers with unsymmetrical Ni–Cl bridging. The Ni–Cl distances are 2.47 and 2.56 Å, the Ni–Cl–Ni angle is 96.55°, and the coordination octahedron is distorted. The single-crystal magnetic susceptibilities have been determined between 1.5 and 25 K and confirm the earlier report of ferromagnetic intradimer exchange interaction. The parameters resulting are: $\langle g \rangle = 2.25$, $D/k = 14 \pm 1$ K, $J/k = 5.0 \pm 0.5$ K, and $zJ'/k = -0.3 \pm 0.1$ K.

The compound di-μ-chloro-tetrakis(ethylenediamine)dinickel(II) chloride, $[Ni_2(en)_4Cl_2]Cl_2$, has been of importance in the development of our ideas about exchange interaction in dimers.[2] Specifically, measurements of the susceptibility over a wide temperature interval provided results which were interpreted in terms of a ferromagnetic intradimer exchange interaction.[3] The superexchange mechanism was also discussed in terms of Anderson's expanded orbital theory.[3,4] Zero-field-splitting effects, which are of dominant importance in nickel(II) chemistry and physics,[5] were explored, but it was not possible to determine the sign of the zero-field-splitting parameter, D, unambiguously. Partly, this was due to the fact that the effect of D on the dimer susceptibility is qualitatively similar to that of an antiferromagnetic interdimer interaction; the earlier measurements were also made only on powdered material. We thought it would be useful to determine the single-crystal susceptibilities of $[Ni_2(en)_4Cl_2]Cl_2$ at low temperatures, in the hope this might resolve some of the remaining ambiguities. Thus, we report here our measurements between 1.5 and 25 K on oriented single crystals. In order to interpret the magnetic studies, it was also necessary first to determine accurately the crystal structure at ambient

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Table I. Positional and Thermal Parameters[a] and Their Estimated Standard Deviations for $[Ni_2(en)_4Cl_2]Cl_2$

atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Ni	0.28201 (4)	0.87917 (2)	0.43585 (2)	0.01182 (6)	0.00395 (2)	0.00264 (1)	−0.00044 (5)	0.00615 (4)	−0.00040 (2)
Cl(1)	0.71799 (8)	0.90110 (4)	0.52657 (3)	0.0123 (1)	0.00481 (3)	0.00402 (2)	−0.0001 (1)	0.00747 (6)	−0.00148 (4)
Cl(2)	0.36695 (10)	1.14525 (6)	0.19988 (4)	0.0280 (2)	0.00615 (4)	0.00517 (2)	0.0067 (1)	0.01342 (8)	0.00355 (5)
N(1)	−0.0854 (3)	0.8949 (1)	0.3543 (1)	0.0140 (4)	0.0049 (1)	0.00386 (7)	−0.0019 (4)	0.0081 (2)	−0.0015 (2)
N(4)	0.2786 (3)	0.9070 (2)	0.3046 (1)	0.0171 (4)	0.0056 (1)	0.00339 (7)	−0.0011 (4)	0.0079 (3)	0.0001 (2)
N(5)	0.2901 (3)	0.6946 (2)	0.4167 (1)	0.0227 (4)	0.0048 (1)	0.00382 (6)	−0.0007 (4)	0.0109 (2)	−0.0011 (2)
N(8)	0.2642 (3)	0.8262 (2)	0.5588 (1)	0.0163 (4)	0.0058 (1)	0.00348 (6)	0.0019 (4)	0.0088 (2)	−0.0005 (2)
C(2)	−0.1334 (3)	0.9498 (2)	0.2629 (1)	0.0166 (5)	0.0064 (2)	0.00377 (9)	0.0024 (5)	0.0059 (3)	−0.0001 (2)
C(3)	0.0303 (4)	0.8932 (2)	0.2292 (1)	0.0214 (6)	0.0072 (2)	0.00294 (9)	0.0021 (5)	0.0059 (3)	−0.0002 (2)
C(6)	0.3583 (5)	0.6385 (2)	0.5092 (2)	0.0345 (7)	0.0051 (2)	0.00515 (10)	0.0080 (6)	0.0147 (4)	0.0026 (2)
C(7)	0.2223 (4)	0.6978 (2)	0.5543 (1)	0.0304 (6)	0.0068 (2)	0.00484 (8)	0.0008 (6)	0.0161 (3)	0.0021 (2)

atom	x	y	z	B, Å^2	atom	x	y	z	B, Å^2
H(11)	−0.147 (4)	0.942 (2)	0.383 (1)	3.1 (5)	H(51)	0.374 (4)	0.680 (2)	0.391 (2)	3.5 (5)
H(12)	−0.146 (4)	0.833 (2)	0.348 (2)	3.4 (5)	H(52)	0.156 (4)	0.667 (2)	0.380 (1)	2.9 (5)
H(21)	−0.094 (4)	1.024 (2)	0.275 (1)	2.9 (5)	H(61)	0.315 (4)	0.551 (3)	0.502 (2)	4.5 (6)
H(22)	−0.308 (4)	0.932 (2)	0.214 (2)	3.4 (5)	H(62)	0.553 (6)	0.646 (3)	0.553 (3)	7.4 (10)
H(31)	0.003 (4)	0.927 (2)	0.170 (2)	3.4 (5)	H(71)	0.276 (5)	0.667 (3)	0.618 (2)	5.2 (7)
H(32)	−0.010 (4)	0.815 (2)	0.215 (1)	2.7 (5)	H(72)	0.046 (4)	0.685 (2)	0.511 (2)	3.6 (5)
H(41)	0.356 (4)	0.976 (2)	0.302 (2)	4.1 (6)	H(81)	0.154 (5)	0.854 (2)	0.555 (2)	3.6 (6)
H(42)	0.379 (5)	0.847 (2)	0.300 (2)	4.3 (6)	H(82)	0.401 (5)	0.850 (2)	0.620 (2)	4.4 (7)

[a] The form of the anisotropic thermal parameter is $\exp[-(h^2\beta_{11}{}^2 + k^2\beta_{22}{}^2 + l^2\beta_{33}{}^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

temperatures.[6] The results of those studies are also reported here.

Experimental Section

The compound was prepared as before.[3] Single crystals were grown by slow evaporation of methanolic solutions. Anal. Calcd for $NiC_4H_{16}N_4Cl_2$: Ni, 23.50; C, 19.23; H, 6.46; N, 22.43; Cl, 28.38. Found (commercially): Ni, 23.28; C, 19.10; H, 6.79; N, 22.11; Cl, 28.14.

Single-crystal susceptibilities were determined between 1.5 and 25 K by the mutual inductance procedure as used earlier in this laboratory.[7,8] Measurements were made parallel to the *a*, *b*, and *c** axes, the crystals (typical weight 100–150 mg) being oriented by X-ray precession camera techniques. The *c** axis is defined as being perpendicular to the *ab* plane.

Crystal data for $[Ni_2(en)_4Cl_2]Cl_2$: $Ni_2Cl_4N_8C_8H_{32}$ mol wt 500, space group $P2_1/c$, $Z = 2$, $a = 6.327$ (3) Å, $b = 11.311$ (2) Å, $c = 15.811$ (4) Å, $\beta = 117.81°$, $V = 1001$ Å^3, $d_{\text{calcd}} = 1.66$ g cm^{-3}, $d_{\text{obsd}} = 1.66$ g cm^{-3}, $\mu(\text{Mo K}\alpha) = 24.1$ cm^{-1}. The crystal dimensions (distances, in mm, of faces from centroid) were $(\bar{1}02)$ 0.24, $(10\bar{2})$ 0.24, (011) 0.1, $(0\bar{1}\bar{1})$ 0.1, $(01\bar{1})$ 0.36, $(0\bar{1}1)$ 0.36; maximum and minimum transmission coefficients were 0.73 and 0.39.

The Enraf-Nonius program SEARCH was used to obtain 25 accurately centered reflections which were then used in the program INDEX to obtain approximate cell dimensions and an orientation matrix for data collection. Refined cell dimensions and their estimated standard deviations were obtained from least-squares refinement of 28 accurately centered reflections. The mosaicity of the crystal was examined by the ω-scan technique and judged to be satisfactory.

Collection and Reduction of the Data. Diffraction data were collected at 292 K on an Enraf-Nonius four-circle CAD-4 diffractometer controlled by a PDP8/M computer, using Mo Kα radiation from a highly oriented graphite-crystal monochromator. The θ–2θ scan technique was used to record the intensities for all nonequivalent reflections for which $1° < 2\theta < 52°$. Scan widths (SW) were calculated from the formula $SW = A + B \tan\theta$, where A is estimated from the mosaicity of the crystal and B allows for the increase in width of a peak due to Kα_1–Kα_2 splitting. The values of A and B were 0.60 and 0.35°, respectively. The calculated scan angle is extended at each side by 25% for background determination (BG1 and BG2). The net count is then calculated as NC = TOT − 2(BG1 + BG2), where TOT is the integrated peak intensity. Reflection data were considered insignificant if intensities registered less than 10 counts above background on a rapid prescan, such reflections being rejected automatically by the computer.

The intensities of four standard reflections, monitored at 100-reflection intervals, showed no greater fluctuations during the data collection than those expected from Poisson statistics. The raw intensity data were corrected for Lorentz–polarization effects (including the polarization effect of the crystal monochromator) and then for absorption. After averaging of the intensities of equivalent reflections, the data were reduced to 1530 independent intensities of which 1465 had $F_o{}^2 > 3\sigma(F_o{}^2)$, where $\sigma(F_o{}^2)$ was estimated from counting statistics.[9] These data were used in the final refinement of the structural parameters.

Determination and Refinement of the Structure. The positions of the nickel and halogen atoms were obtained from a three-dimensional Patterson synthesis calculated from all intensity data. The positions of the remaining nonhydrogen atoms were determined from a Fourier difference function.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. The weights w were then taken as $[2F_o/\sigma(F_o{}^2)]^2$, where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. The atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber,[10] and those for hydrogen were taken from Stewart et al.[11] The effects of anomalous dispersion for all nonhydrogen atoms were included in F_c using the values of Cromer and Ibers[12] for $\Delta f'$ and $\Delta f''$. Agreement factors are defined as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$. The principal programs used have been described.[13]

A Fourier difference function now located all of the hydrogen atoms. Anisotropic temperature factors were introduced for all nonhydrogen atoms, and full-matrix least squares was carried out on all parameters including those for the hydrogen atoms. The hydrogen atom positions were included in the refinement for three cycles and subsequently held fixed. The model converged with $R = 2.8$ and $R_w = 3.9\%$. The largest parameter shift at convergence was less than one-tenth of its estimated standard deviation. A structure factor calculation with all observed and unobserved reflections included (no refinement) gave $R = 3.5\%$; on this basis it was decided that careful measurement of reflections rejected automatically during data collection would not significantly improve the results. A final Fourier difference function was featureless. Tables of the observed structure factors are available.[14]

Results and Discussion

Final positional and thermal parameters for $[Ni_2(en)_4Cl_2]Cl_2$ are given in Table I. Tables II and III contain the bond lengths and angles. The digits in parentheses in the tables are the estimated standard deviations in the least significant figures quoted and were derived from the inverse matrix in the course of least-squares refinement calculations. Figure 1 shows a stereoscopic pair view of $[Ni_2(en)_4Cl_2]Cl_2$ and Figure 2 shows the molecular packing in the unit cell.

The complex consists of chlorine-bridged cationic $[Ni(en)_2Cl]_2{}^{2+}$ dimers and uncoordinated Cl^- anions. The nearest interionic contacts are between the chloride anions and the H atoms of ligand amino groups (Table IV). The Cl^- anions are positioned in the lattice so as to permit weak hydrogen-

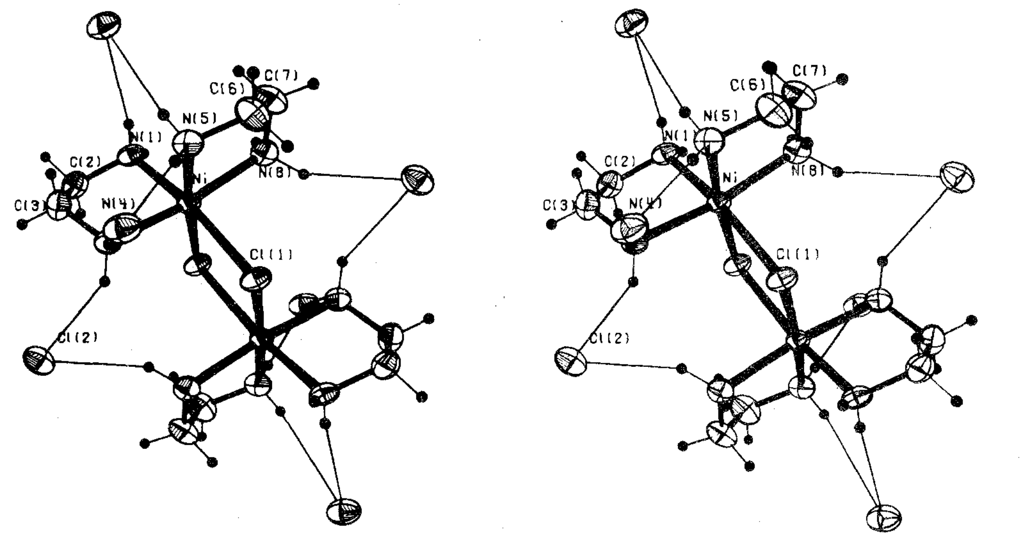

Figure 1. Stereoview of $[Ni_2(en)_4Cl_2]Cl_2$.

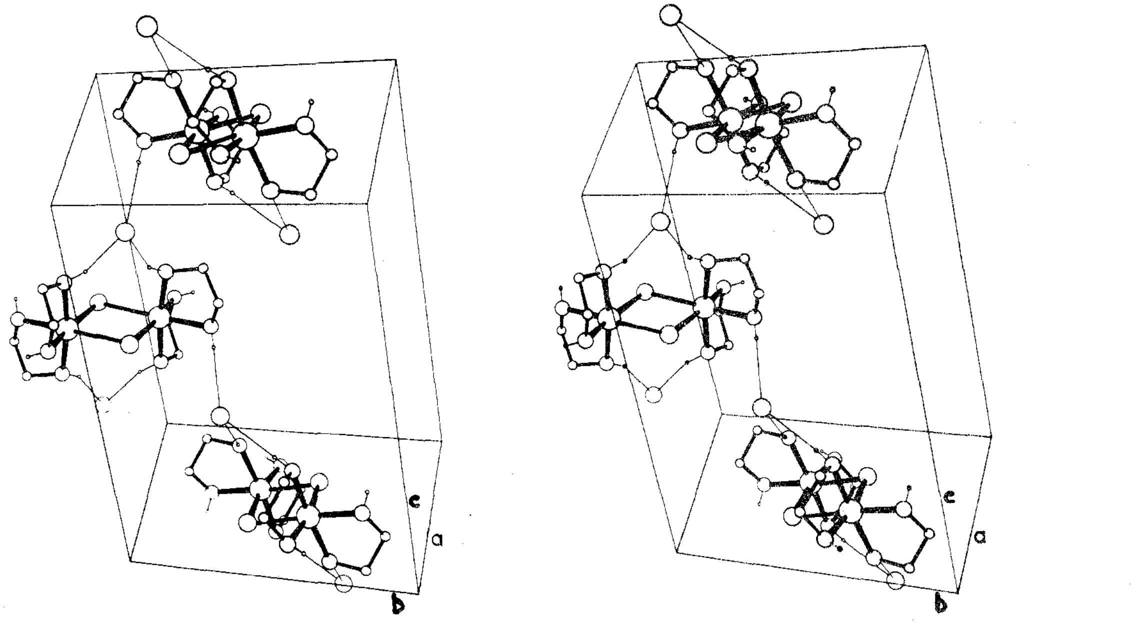

Figure 2. Stereoview of the molecular packing.

Table II. Bond Distances and Selected Intramolecular Distances (Å)

Ni-Cl(1)	2.471 (1)	N(4)-C(3)	1.484 (2)
Ni-Cl(1′)	2.561 (1)	N(5)-C(6)	1.471 (2)
Ni-N(1)	2.087 (1)	N(8)-C(7)	1.474 (2)
Ni-N(4)	2.089 (1)	C(2)-C(3)	1.511 (2)
Ni-N(5)	2.117 (1)	C(6)-C(7)	1.509 (2)
Ni-N(8)	2.095 (1)	Ni-Ni′	3.756 (1)
N(1)-C(2)	1.477 (2)	Cl(1)-Cl(1′)	3.349 (1)

bonding interactions with amino hydrogen atoms of the ethylenediamine ligands, as shown in the figures. This weak interaction links the anions and cations into a polymeric network.

The ligand environment about the nickel atoms is approximately octahedral with some trigonal and slight tetragonal distortion. The bite angles of the ethylenediamine ligands at the nickel atom average 82.5°; a regular octahedron requires 90°. The same is true of the Cl(1)-Ni-Cl(1′) angle (83.5°). The Ni-Cl bridging is unsymmetrical: one of the Ni-Cl bonds is 0.09 Å longer than the other. On the opposite side, the Ni-N(5) bond is elongated by 0.023 Å over the average of the other three Ni-N bonds, completing the tetragonal elongation along the Cl(1′)-Ni-N(5) axis. The angle of trigonal twist ϕ (of opposite octahedral faces) is 51.18°, vs. the 60° of a perfect octahedron (Figure 3).

Table III. Bond Angles (deg)

Cl(1)-Ni-Cl(1′)	83.45 (1)	N(4)-Ni-N(5)	89.75 (5)
Cl(1)-Ni-N(1)	169.10 (3)	N(4)-Ni-N(8)	171.35 (5)
Cl(1)-Ni-N(4)	93.60 (3)	N(5)-Ni-N(8)	82.32 (4)
Cl(1)-Ni-N(5)	95.10 (3)	Ni-Cl(1)-Ni	96.55 (1)
Cl(1)-Ni-N(8)	90.55 (3)	Ni-N(1)-C(2)	108.23 (9)
Cl(1′)-Ni-N(1)	86.68 (3)	Ni-N(4)-C(3)	108.01 (9)
Cl(1′)-Ni-N(4)	94.82 (4)	Ni-N(5)-C(6)	107.37 (9)
Cl(1′)-Ni-N(5)	175.28 (3)	Ni-N(8)-C(7)	108.85 (8)
Cl(1′)-Ni-N(8)	93.19 (3)	N(1)-C(2)-C(3)	107.8 (1)
N(1)-Ni-N(4)	82.60 (5)	N(4)-C(3)-C(2)	108.3 (1)
N(1)-Ni-N(5)	95.10 (5)	N(5)-C(6)-C(7)	108.2 (1)
N(1)-Ni-N(8)	94.62 (5)	N(8)-C(7)-C(6)	109.5 (1)

Table IV. Closest Interionic (Hydrogen) Contacts (Å)

atom 1	H atom	atom 2	D^a	d^b
Cl(2)	H(12)	N(1)	3.242 (1)	2.468 (1)
Cl(2)	H(41)	N(4)	3.349 (1)	2.356 (1)
Cl(2)	H(42)	N(4)	3.349 (1)	2.795 (1)
Cl(2)	H(51)	N(5)	3.486 (1)	2.664 (1)
Cl(2)	H(82)	N(8)	3.467 (1)	2.540 (1)

[a] Atom 1 to atom 2. [b] Atom 1 to H atom.

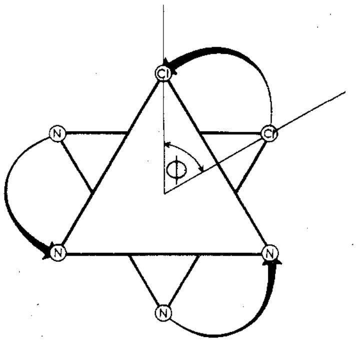

Figure 3. Definition of the angle of trigonal twist ϕ.

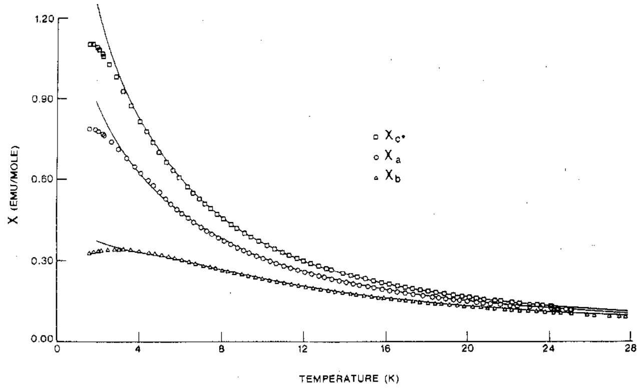

Figure 4. Experimental susceptibilities (points) and calculated fits to the data.

There are several other Ni–Cl–Ni bridged structures related to the present system. The doubly bridged (but five-coordinate) $Ni_2Cl_8^{4-}$ anion has shorter Ni–Cl bonds (2.38 and 2.46 Å vs. 2.47, and 2.56 Å in the present study) and a slightly larger bridging angle.[15] Triply bridged octahedra are found[16] in linear chains in $(CH_3NH_3)NiCl_3$, and this causes the Ni–Cl bonds to be shorter (2.35, 2.35, 2.41 Å) and also results in much smaller bridging Ni–Cl–Ni angles (78.5, 78.5, 76.4°). All these materials have unsymmetrical Ni–Cl–Ni bridges.

The experimentally determined susceptibilities are reported in Figure 4. Their interpretation has been hindered by the fact that, as recently reported,[17] a crystal phase transition of $[Ni_2(en)_4Cl_2]Cl_2$ occurs at low temperatures. A broad peak in the heat capacity was found between 10 and 27 K, and X-ray diffraction powder diagrams show that the monoclinic crystal becomes triclinic in that temperature interval, which of course is the temperature region in which the presently reported data have been obtained. We have adopted the point of view that molecule motion may occur during the transition but that, since it occurs at such low temperatures, no drastic reorientation of the relatively large dimeric molecule occurs. Crystals that had been cooled to low temperatures were found, upon being removed from the cryostat, not to have shattered. Instead of choosing an axis of quantization on the basis of the room-temperature structure of the system, we have thus chosen to allow the orientation of that axis also to be a fitted parameter. Given the distorted structure of the molecule at room temperature as well as the monoclinic space group, we would have been required to use this procedure anyway. An earlier example of this procedure was provided by $NiCl_2 \cdot 4H_2O$.[7]

Table V. Magnetic Parameters for $[Ni_2(en)_4Cl_2]Cl_2$

	A^a	B^b	C^b
$\langle g \rangle$	2.25 ± 0.02	2.14	2.12
D/k, K	14 ± 1	9.4	−16
J/k, K	5.0 ± 0.5	14.2	15.0
zJ'/k, K	−0.3 ± 0.1	−0.24	−0.03
C_{bz}^2	0.0745		
C_{az}^2	0.3612		

[a] Best fitted values, this work. [b] The two best fits of the powder data as reported in ref 3.

The spin Hamiltonian chosen for the analysis is given by eq 9 of ref 3

$$\mathcal{H} = -2JS_1 \cdot S_2 - D(S_{1z}^2 + S_{2z}^2) - g_i\mu_B H \cdot S_i \qquad (1)$$

where $i = x$, y, or z. The term in D represents the usual zero-field splitting of the $^3A_2$ ground state of nickel(II), with the sign convention that a positive D corresponds to the doublet being below the singlet. The expressions for the susceptibility were derived earlier[3] and are so lengthy that they are not reproduced here. We have used χ_x, χ_y, and χ_z as defined by eq 13 and 14 of ref 3. We have allowed for an interdimer exchange term in the molecular field approximation[18] which yields the exchange-corrected susceptibility, χ_i', as

$$\chi_i' = \frac{\chi_i}{1 - (2zJ'/Ng^2\mu_B^2)\chi_i} \qquad (2)$$

where i refers again to the set (x, y, or z).

The susceptibilities for directions parallel to the crystal axes a, b, or c^* were calculated by using these exchange-corrected susceptibilities (eq 2) and by introducing as fitting parameters the direction cosines of the crystal axes with respect to the molecular z axis. Thus, $\chi_x = \chi_y$, by assuming axial symmetry, and

$$\chi_j' = C_{jz}^2\chi_z' + (1 - C_{jz}^2)\chi_x' \qquad (3)$$

$j = a$, b, or c^*, where C_{jz} is the direction cosine between the j axis and z axis. The data were fitted to eq 3 with isotropic g values, which is common for nickel.

This procedure resulted in a good fit to the data between 2.5 and 25 K with the parameters which are given in Table V. Since the fits of data were insensitive to the sign of the direction cosines, the molecular z axis was not able to be oriented with respect to the crystal axis. For comparison, the results reported earlier[3] are also listed.

It is clear from these results that there is a relatively large single-ion zero-field splitting, with the doublet lying lower. Earlier measurements[3] could not resolve the sign of D, but a satisfactory fit to the data presented here could not be obtained with a negative value for D. The intradimer exchange constant is smaller than that reported earlier,[3] as was recently suggested,[17] but the sign remains ferromagnetic. The value for $\langle g \rangle$ obtained here is more typical of that usually found for nickel, and there is a small antiferromagnetic interdimer interaction. In fact, the data (Figure 4) may be seen to level off at the lowest temperatures achieved here (1.5 K), suggesting that long-range order may occur at slightly lower temperatures.

It is interesting to note how closely the magnetic parameters reported here for a $[Ni(Cl)_2Ni]$ dimer unit compare with those reported[19] for the $[Ni(Cl)_2Ni]_\infty$ linear chains which occur, for example, in $NiCl_2 \cdot 2py$. The intrachain exchange parameter in this compound likewise is ferromagnetic in sign, $J/k = 5.35$ K, and D/k is even larger than that reported here, 27 K. It is indeed satisfying that the magnetic properties for this structural unit appear to be more or less independent of the number of the units joined together, which is consistent with the chemical and geometric features being generally quite similar.

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Registry No. $[Ni_2(en)_4Cl_2]Cl_2$, 20647-35-2.

Supplementary Material Available: A listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Properties and Structures of the Five-Coordinate Copper(II) and Six-Coordinate Nickel(II) Complexes $\{[CuL]\cdot 2H_2O\}_\infty$ and $[NiLH_2O]_2$, L = *N,N'*-Bis[(2-hydroxy-5-methylphenyl)(4-methylphenyl)methylene]-3-azahexane-1,6-diamine

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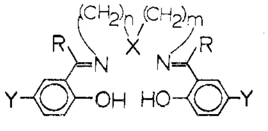
The copper(II) and nickel(II) complexes of the potentially pentadentate ligand (2,3-mmbpN) derived from the Schiff base condensation of 3-azahexane-1,6-diamine and 5,4'-dimethyl-2-hydroxybenzophenone have been synthesized and their crystal structures and magnetic and spectral properties determined. For comparison, the copper and nickel complexes of a series of related ligands have also been synthesized and their magnetic and spectral properties determined. The ligands act as pentadentates, in contrast with the coordination reported for some analogous Schiff base ligands with salicylaldehyde. The structures of both the copper and nickel complexes with 2,3-mmbpN are unexpected. The copper environment is very close to trigonal bipyramidal, with the amine nitrogen bond being only 0.1 Å longer than the imine nitrogen bonds. This amine nitrogen bond, at 2.077 Å, is much shorter than the analogous bond in the related complexes [Cu(3,3-mbpN)] (2.374 Å) and [Cu(3,4-cbpN)] (2.291 Å), and this shortening is ascribed to the steric requirements of the ligand. The nickel environment is close to octahedral, with a molecule of water coordinated to the nickel in a position cis to the amine nitrogen. Such coordination has been previously observed for complexes of cobalt(III) but not for nickel(II). The hydrogen bonding links neighboring molecules to form weakly linked dimers in the nickel complex, $[Ni(2,3\text{-mmbpN})\cdot H_2O]_2$, and infinite chains in the copper complex, $\{[Cu(2,3\text{-mmbpN})]\cdot 2H_2O\}_\infty$. The crystal structures were determined from full-matrix least-squares refinement of counter data: $[Cu(2,3\text{-mmpbN})]\cdot 2H_2O$, space group $C2/c$, $Z = 4$, $a = 29.128$ Å, $b = 8.503$ (2) Å, $c = 13.921$ (5) Å, $\beta = 106.63$ (2)°, $V = 3304$ Å^3, $R = 3.5\%$ for 1718 reflections; $[Ni(2,3\text{-mmbpN})H_2O]$, space group $P\bar{1}$, $Z = 2$, $a = 10.833$ (2) Å, $b = 12.63$ (1) Å, $c = 13.137$ (6) Å, $\alpha = 116.83$ (5)°, $\beta = 91.09$ (4)°, $\gamma = 93.91$ (6)°, $V = 1598$ Å^3, $R = 3.1\%$ for 3118 reflections.

Introduction

A series of bivalent and trivalent metal complexes with pentadentate Schiff base ligands of type **1** have shown an interesting range of structures and properties. In particular, indirect structural studies on the ligand $salXH_2$ (R = H, X = NH, NC_6H_5, S, O, PCH_3, Y = H) have suggested structures in which the donor X was frequently uncoordinated.[2-4] On the other hand, analogous ligands based on substituted *o*-hydroxybenzophenones ($R = C_6H_5$) have to date always yielded complexes in which the ligand acts as a pentadentate, with X coordinated to the metal.[5-10] Comparison of spectral and magnetic properties suggests that in a few specific cases, the salX complexes also have the donor X coordinated. There is in fact no reason why the salicylaldehyde and benzophenone derivatives should behave differently in this respect, except for differences in ligand electronegativities. To date, attempts to obtain X-ray evidence for complexes with the donor atom X uncoordinated have not been successful. Complexes with ligands (**1**) acting as pentadentates have the phenolic oxygen atoms either cis or trans to each other and the mechanism that makes one structure preferred over the other is not yet clear. The differences appear to be small between the ligands of complexes adopting different structural types. In particular, completed and preliminary X-ray studies show that [M(3,3-cbpN)] (M = Ni, Cu, Zn), [M(3,4-cpbN)] (M = Ni,



1: *n,m*-$salH_2$, R, Y = H; *n,m*-$cbpH_2$, $R = C_6H_5$, Y = Cl; *n,m*-$mbpH_2$, $R = C_6H_5$, $Y = CH_3$; *n,m*-$mmbpH_2$, R = *p*-$CH_3C_6H_4$, $Y = CH_3$

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