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Crystal and Molecular Structures of the Nickel and Cobalt Dichlorobis(diarsine)metal Monochlorides

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The crystal and molecular structures of the complexes dichlorobis(diarsine)nickel monochloride ($C_{20}H_{32}As_4Cl_3Ni$) and dichlorobis(diarsine)cobalt monochloride ($C_{20}H_{32}As_4Cl_3Co$) have been determined from single-crystal X-ray data collected on an automated diffractometer. The structures have been refined by least squares to an R index of 0.038 for 1500 reflections of nonzero weight in the case of nickel and to an R index of 0.033 for 1424 reflections for the cobalt structure. The compounds are approximately isostructural. The crystals are monoclinic, space group $P2_1/c$, with cell dimensions $a = 9.170 \pm 0.007$ Å, $b = 9.592 \pm 0.005$ Å, $c = 14.986 \pm 0.003$ Å, $\beta = 97.96 \pm 0.07°$ for the nickel complex, and $a = 9.180 \pm 0.002$ Å, $b = 9.589 \pm 0.001$ Å, $c = 14.970 \pm 0.003$ Å, $\beta = 97.98 \pm 0.02°$ for the cobalt complex. The calculated density for both compounds is 1.87 g cm^{-3} for two molecules per unit cell, in good agreement with the observed values of 1.84 g cm^{-3} and 1.86 g cm^{-3}. The monocation $M(diars)_2Cl_2^+$ (M = Ni, Co; diars = $o\text{-}C_6H_4(As(CH_3)_2)_2$) is monomeric and centrosymmetric. The four arsenic atoms are in a square-planar arrangement about the metal atom with the two chlorine atoms completing a slightly distorted octahedron. The metal–arsenic distances are Ni–As = 2.342 (2) and Co–As = 2.334 (2) Å. The most important difference between the two structures is in the M–Cl bond length which is 2.425 (3) Å for Ni–Cl and 2.256 (3) Å for Co–Cl. The larger value for the Ni–Cl distance is probably due to the presence of an unpaired electron in the d_{z^2} orbital.

Introduction

The ligand *o*-phenylenebis(dimethylarsine) (diarsine or diars = $o\text{-}C_6H_4(As(CH_3)_2)_2$) has assumed a major role in coordination chemistry. Of particular interest is the fact that diarsine is found in many complexes which possess unusual ground electronic states. Notable examples are the spin-triplet $Fe(diars)_2Cl_2^{2+}$ [1] and the spin-doublet $Ni(diars)_2Cl_2^+$ [2] complexes.

We have begun an extensive investigation of the spectroscopic and magnetic behavior of several diarsine complexes, with the goal of elucidating the key features of their electronic structures. In order to carry out significant studies of electronic structure, a substantial supply of crystal and molecular structural information is needed. Unfortunately, there is a paucity of such data. For example, of all the interesting nickel complexes containing diarsine, only the structures of the diamagnetic complexes $Ni(diars)_2I_2$[3] and $[Ni(diars)(triars)](ClO_4)_2$[4] have been reported. Therefore, we have determined the crystal and molecular structures of $[Ni(diars)_2Cl_2]Cl$ and $[Co(diars)_2Cl_2]Cl$. The results of this investigation are presented in this paper.

Experimental Section

The compounds $[Ni(diars)_2Cl_2]Cl$ and $[Co(diars)_2Cl_2]Cl$ were prepared by the methods of Nyholm[2,5] and recrystallized from ethanol. The nickel crystals were small golden-brown rectangular parallelepipeds, elongated along the a axis. The cobalt crystals were bright green rhombus-shaped plates with principal face {100}. The space group in both cases was determined from $h0l$ and $0kl$ Weissenberg photographs. The cell dimensions were determined by least-squares fits to 12 reflections measured on a Datex-automated General Electric diffractometer using Co Kα radiation (λ 1.79021 Å). Both crystals are monoclinic with space group $P2_1/c$ ($h0l$ absent for l odd, $0k0$ absent for k odd). The cell dimensions for $[Ni(diars)_2Cl_2]Cl$ are $a = 9.170 \pm 0.07$ Å, $b = 9.592 \pm 0.005$ Å, $c = 14.986 \pm 0.003$ Å, and $\beta = 97.96 \pm 0.07°$; for $[Co(diars)_2Cl_2]Cl$ they are $a = 9.180 \pm 0.002$ Å, $b = 9.589 \pm 0.001$ Å, $c = 14.970 \pm 0.003$ Å, and $\beta = 97.98 \pm 0.02°$. The densities measured by flotation in xylene and methylene diiodide are 1.84 g/cm^3 for the nickel compound and 1.86 g/cm^3 for the cobalt compound; in both cases the density calculated for two molecules in the cell is 1.87 g/cm^3.

Initial intensity data for the nickel compound were obtained from multiple-film Weissenberg photographs prepared using Cu Kα radiation. Additional data were collected on both compounds using a Datex-automated General Electric diffractometer and iron-filtered cobalt X-radiation. Intensities were measured using a θ–2θ scan speed of 2°/min. Background was counted for 30 sec before and after each scan.

For the nickel compound all reflections within a quadrant of reciprocal space out to $2\theta = 155°$ were measured; the scan range varied linearly from 2.08° at $2\theta = 4°$ to 4.38° at $2\theta = 155°$. Two moderately strong check reflections, 080 and 544, were remeasured alternately every 20 reflections; they showed no significant drift during the seven days of 24 hr operation. A total of 1731 independent reflections were measured, of which 40 had net counts less than zero.

For the cobalt compound, data were collected out to $2\theta = 130°$; the scan range varied from 1.93° at $2\theta = 4°$ to 3.00° at $2\theta = 130°$. The check reflections were 008 and 446. Of the 1424 measured intensities, 22 were less than zero. The reflections were recorded twice but only the first set of data was used in the refinement because of indications that the mosaicity of the crystal was changing during the measurements. The counts of the stronger reflections increased with time by amounts reaching up to 8–10%, indicating a reduction in secondary extinction as the result of increased mosaicity. Subsequent least-squares refinement showed that secondary extinction was indeed an important factor for the cobalt crystal. No attempt was made to correct for the apparent change in secondary extinction during the data collection.

The initial processing of the data consisted of the assignment of a standard deviation to each reflection, corrections for Lorentz and polarization factors, and the scaling of the reflections[6] to give values of F^2 and $\sigma(F^2)$ for all reflections (including those having negative net intensities). The assigned variances $\sigma^2(I)$ contained, besides counting statistics, a term $(0.02S)^2$ where S is the scan count. These variances were the basis of the weights used in the least-squares refinement.

No absorption corrections were made. The crystal of $Ni(diars)_2Cl_3$ measured approximately 0.2 × 0.13 × 0.06 mm and has an absorption coefficient for Co Kα of $\mu = 156$ cm^{-1}; the crystal of $Co(diars)_2Cl_3$ was about 0.1 mm on an edge and $\mu = 155$ cm^{-1}. Possible ramifications of absorption effects are discussed later.

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(1) R. V. Parish and R. S. Nyholm, *Chem. Ind. (London)*, 470 (1956).

(2) R. S. Nyholm, *J. Chem. Soc.*, 851, 2061 (1950).

(3) N. C. Stephenson, *Acta Crystallogr.*, **17**, 592 (1964).

(4) B. Bosnich, R. S. Nyholm, and P. J. Pauling, and M. L. Tobe, *J. Amer. Chem. Soc.*, **90**, 4741 (1968).

(5) R. S. Nyholm, *J. Chem. Soc.*, 851, 2071 (1950).

(6) A. J. C. Wilson, *Nature (London)*, **150**, 151 (1942).

TABLE I

FINAL COORDINATES AND TEMPERATURE PARAMETERS OF THE HEAVIER ATOMS[a]

	x	y	z	b_{11}	b_{22}	b_{33}	b_{12}	b_{13}	b_{23}
				(a) Ni Compound					
Ni	0	0	0	59 (2)	26 (1)	17 (0.5)	−3 (3)	6 (2)	−2 (1)
As(1)	1987 (1)	1511 (0.6)	−60 (0.4)	55 (1)	28 (0.7)	18 (0.3)	−13 (1)	3 (1)	−2 (0.6)
As(2)	769 (1)	−1166 (0.6)	−1229 (0.4)	69 (1)	29 (0.7)	21 (0.3)	−14 (1)	13 (1)	−10 (0.6)
Cl(1)	1424 (2)	−1498 (2)	1098 (1)	95 (3)	49 (2)	30 (0.7)	10 (4)	−16 (2)	27 (2)
Cl(2)	$^1/_2$	0	$^1/_2$	96 (5)	92 (3)	33 (1)	79 (6)	25 (4)	16 (3)
C(1)	2766 (8)	1142 (6)	−1178 (4)	42 (11)	48 (6)	20 (3)	9 (13)	4 (8)	13 (6)
C(2)	2210 (8)	19 (6)	−1693 (4)	65 (13)	36 (6)	21 (3)	12 (13)	14 (9)	7 (6)
C(3)	2794 (9)	−300 (6)	−2484 (4)	77 (13)	56 (7)	28 (3)	−5 (15)	16 (10)	−7 (7)
C(4)	3884 (9)	486 (7)	−2743 (4)	99 (15)	77 (8)	27 (3)	27 (17)	43 (10)	12 (8)
C(5)	4482 (9)	1596 (6)	−2223 (4)	86 (13)	73 (7)	28 (3)	−17 (16)	20 (10)	26 (8)
C(6)	3880 (9)	1949 (6)	−1443 (4)	89 (13)	57 (7)	27 (3)	−28 (15)	8 (10)	10 (7)
C(7)	1573 (9)	3480 (6)	−63 (4)	76 (13)	43 (7)	40 (3)	−21 (14)	−22 (11)	−4 (8)
C(8)	3738 (9)	1318 (7)	805 (4)	82 (13)	104 (9)	24 (3)	−4 (16)	−19 (10)	−1 (8)
C(9)	1807 (11)	−2920 (7)	−1038 (5)	175 (20)	50 (8)	54 (4)	36 (19)	84 (13)	2 (9)
C(10)	−678 (9)	−1549 (8)	−2257 (4)	100 (14)	126 (10)	30 (3)	−84 (19)	16 (10)	−55 (9)
				(b) Co Compound					
Co	0	0	0	37 (2)	15 (1)	18 (0.6)	−2 (2)	−3 (2)	1 (1)
As(1)	1980 (0.6)	1504 (0.6)	−65 (0.4)	34 (0.8)	16 (0.8)	19 (0.3)	−13 (1)	1 (0.7)	−2 (0.7)
As(2)	768 (0.6)	−1165 (0.6)	−1223 (0.4)	50 (0.9)	19 (0.8)	21 (0.3)	−13 (1)	14 (0.8)	−11 (0.7)
Cl(1)	1360 (2)	−1390 (2)	1008 (1)	62 (2)	35 (2)	30 (0.7)	10 (3)	−20 (2)	26 (2)
Cl(2)	$^1/_2$	0	$^1/_2$	80 (3)	75 (3)	36 (1)	77 (5)	32 (3)	17 (3)
C(1)	2755 (5)	1144 (5)	−1184 (3)	32 (7)	30 (6)	21 (3)	−20 (11)	−3 (7)	12 (7)
C(2)	2220 (6)	−4 (5)	−1695 (4)	42 (7)	33 (7)	22 (3)	13 (11)	25 (7)	7 (7)
C(3)	2782 (7)	−312 (7)	−2482 (4)	90 (10)	43 (8)	30 (4)	13 (15)	3 (9)	−21 (9)
C(4)	3906 (7)	466 (7)	−2750 (4)	78 (9)	75 (8)	24 (3)	15 (14)	39 (9)	21 (9)
C(5)	4457 (7)	1575 (6)	−2231 (4)	59 (8)	59 (8)	31 (3)	−6 (14)	25 (9)	32 (9)
C(6)	3896 (7)	1925 (7)	−1450 (4)	66 (9)	39 (8)	28 (3)	−10 (13)	−12 (9)	5 (9)
C(7)	1558 (8)	3478 (6)	−90 (5)	72 (10)	20 (7)	48 (4)	−5 (13)	25 (10)	−15 (8)
C(8)	3735 (7)	1339 (8)	803 (5)	53 (9)	80 (10)	32 (4)	−22 (16)	−17 (9)	2 (9)
C(9)	1791 (11)	−2908 (7)	−1043 (7)	132 (13)	44 (8)	66 (5)	62 (17)	94 (15)	6 (11)
C(10)	−669 (8)	−1558 (9)	−2269 (5)	83 (10)	133 (11)	28 (3)	−56 (19)	6 (10)	−66 (10)

[a] Standard deviations are in parentheses. All values are multiplied by 10^4. The temperature factor has the form $\exp(-b_{11}h^2\cdots -b_{12}hk\cdots)$.

Solution and Refinement of the Structures

The positions of the nickel atoms—at centers of symmetry, chosen as 0, 0, 0 and 0, $^1/_2$, $^1/_2$—were confirmed, and the positions of the arsenic atoms were determined from a three-dimensional Patterson map calculated from the photographic data. Positions of the chlorine and carbon atoms were recovered from subsequent electron-density maps. Least-squares refinement including anisotropic temperature factors for the Ni, As, and Cl atoms and isotropic temperature factors for the carbon atoms converged at an R index of 0.14. At this stage we collected the diffractometer data for both compounds.

Further refinement on the nickel compound included anisotropic temperature factors for all nonhydrogen atoms. Hydrogen atoms were then introduced. The positions of the four hydrogen atoms on the benzene ring were assigned assuming sp^2 hybridization and C–H distances of 0.9 Å; the methyl hydrogen atoms were located with the aid of difference Fourier maps calculated in planes perpendicular to the As–C bonds. These methyl hydrogen atoms showed up quite clearly in all four maps, indicating that the methyl groups have ordered conformations. The hydrogen atoms were included in subsequent structure factor calculations, but their positions were not further adjusted.

At a late stage in the refinement, 231 reflections were given zero weight. These reflections fell in the region of reciprocal space $\bar{h}kl$ with, in general, $|h| > 5$. Within this block of data, the stronger intensities showed consistently uneven background counts, the high-angle count being appreciably larger than the low-angle count. Apparently the crystal was either slightly misaligned or had larger mosaicity in this direction.

In the final least-squares cycles, 131 parameters were included in a single matrix: six temperature parameters for the two atoms in spacial positions, three coordinates and six temperature parameters for all other nonhydrogen atoms, a scale factor, and a secondary extinction parameter. The quantity minimized was $\Sigma w(F_o^2 - (F_c^*/K)^2)^2$, with F_c^* as defined by Larson,[7] eq 3, and weights w taken equal to $1/\sigma^2(F_o^2)$. In the last cycle no parameter changed by as much as one-third of its esd. The final R value $(=\Sigma||F_o| - |F_c^*||/\Sigma|F_o|)$ was 0.038 for 1500 reflections, and the goodness of fit was 1.95. The final value of the secondary extinction parameter g was $(5.0 \pm 0.2) \times 10^{-6}$.

Refinement of the cobalt structure proceeded in the same manner, beginning with the parameters found for the nickel compound. The hydrogen atoms of the methyl groups were found on difference Fourier maps, which again indicated no disorder. In this case, the coordinates and isotropic temperature factors for the hydrogen atoms were included in the refinement, for a total of 195 parameters. The final R index for 1424 reflections was 0.033 and the goodness-of-fit 2.3. The final value of g was $(21.1 \pm 0.4) \times 10^{-6}$.

Calculations were carried out on IBM 7094 and IBM 360-75 computers using subprograms of the CRYRM and CRYM systems.[8] Atomic form factors for Ni, Co, As, Cl, and C were taken from the International Tables.[9] For the nickel compound, the form factors of As and Ni were corrected by −1.0 and −2.3 electrons to take account of the real ($\Delta f'$) component of anomalous dispersion; no such corrections were made for the cobalt compound. Form factors for hydrogen were taken from Stewart, Davidson, and Simpson.[10]

Final parameters of the heavy atoms are given in Table I, and of the hydrogen atoms in Table II. Observed and calculated structure factors are available elsewhere.[11]

Description of the Structures

The monocations Ni(diars)$_2$Cl$_2^+$ and Co(diars)$_2$Cl$_2^+$

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[7] A. C. Larson, *Acta Crystallogr.*, **23**, 664 (1967).

[8] D. J. Duchamp, Paper B-14, American Crystallographic Association Meeting, Bozeman, Mont., 1964, p 29.

[9] "International Tables for X-ray Crystallography," Vol. 3, Kynoch Press, Birmingham, England, 1962, Table 3.3.1A.

[10] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).

[11] A listing of observed and calculated structure factors will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-3040. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

TABLE II

PARAMETERS OF THE HYDROGEN ATOMS[a]

		Ni			Co			
Atom	Bonded to	x	y	z	x	y	z	B
H(3)	C(3)	252	−106	−277	249 (6)	−90 (6)	−276 (4)	1.1 (1.4)
H(4)	C(4)	432	34	−314	430 (7)	29 (6)	−324 (4)	2.8 (1.4)
H(5)	C(5)	511	223	−241	520 (7)	205 (7)	−235 (4)	3.0 (1.5)
H(6)	C(6)	429	265	−104	414 (6)	254 (6)	−114 (4)	0.8 (1.3)
H(7)	C(7)	54	361	−42	58 (8)	355 (7)	−52 (4)	3.7 (1.6)
H(7′)		236	396	−37	236 (7)	401 (7)	−24 (4)	2.4 (1.3)
H(7″)		166	379	53	149 (8)	379 (7)	46 (5)	4.4 (1.8)
H(8)	C(8)	433	218	79	442 (8)	204 (8)	71 (5)	4.7 (1.9
H(8′)		426	49	65	416 (7)	55 (7)	71 (4)	3.0 (1.6)
H(8″)		343	127	143	346 (8)	138 (7)	141 (5)	5.5 (2.0)
H(9)	C(9)	258	−281	−53	257 (9)	−287 (8)	−63 (5)	4.9 (2.3)
H(9′)		212	−321	−160	224 (7)	−315 (7)	−153 (5)	3.6 (1.7)
H(9″)		105	−363	−84	103 (9)	−361 (8)	−94 (5)	5.5 (2.0)
H(10)	C(10)	−117	−67	−242	−148 (10)	−88 (10)	−238 (6)	9.7 (3.0)
H(10′)		−129	−232	−209	−131 (7)	−234 (7)	−198 (4)	3.9 (1.5)
H(10″)		−5	−184	−277	−15 (10)	−194 (10)	−276 (6)	7.9 (2.4)

[a] Coordinates are multiplied by 10^3. For the nickel compound, hydrogen positions were assigned from difference maps and geometric considerations, and the isotropic temperature factor B was taken as 4.0 for all hydrogens. For the cobalt compound, the parameters were included in the least-squares refinement, and standard deviations are given in parentheses.

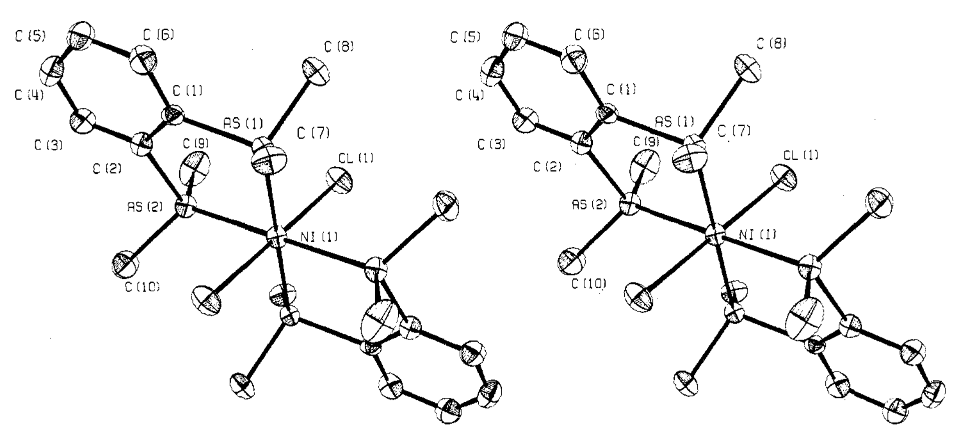

Figure 1. A stereoscopic view of the $Ni(diars)_2Cl_2^+$ cation, looking down the $\vec{b}$ axis.

are monomeric and centrosymmetric; a drawing of the nickel cation is shown in Figure 1. Four arsenic atoms surround the metal atom in an approximately square-planar arrangement, and two chlorine atoms complete a slightly distorted octahedron.

The cations have approximate C_{2h} $(2/m)$ symmetry, with the mirror planes passing through the chlorine atoms and the midpoints of the C(4)–C(5) bonds. Distortions from the ideal symmetry D_{2h} (mmm) are reflected in displacements of the chlorine atoms from the axial positions by about three degrees and in foldings, about the lines As(1)···As(2), of the benzene rings relative to the metal–arsenic planes; the dihedral angles about this fold are about 9° in both cations. These distortions help to relieve crowding between the chlorine atoms and methyl groups; each chlorine atom is surrounded by four methyl groups, with Cl···C distances of 3.50–3.56 Å in the nickel cation and 3.44–3.51 Å in the cobalt cation. The crowding is also relieved by expansion of the M–As–CH_3 angles from the tetrahedral value to nearly 120° (see Table IV). Completely analogous but slightly larger distortions are found in crystals of the neutral molecule $Ni(diars)_2I_2$,[3] although in that case they were attributed (erroneously, we believe) to intermolecular forces.

A packing drawing of the nickel compound is shown in Figure 2. The most interesting interionic contact

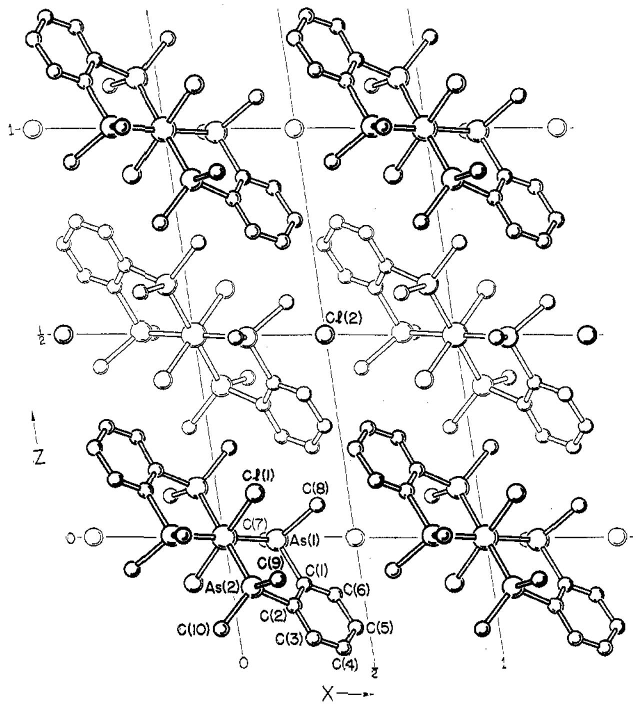

Figure 2.—A packing diagram of the $[Ni(diars)_2Cl_2]Cl$ unit cell, looking up the $\vec{b}$ axis.

TABLE III
BOND DISTANCES (Å)[a]

	M = Ni	M = Co
M–As(1)	2.339 (3)	2.333 (3)
M–As(2)	2.345 (3)	2.336 (3)
M–Cl(1)	2.425 (3)	2.256 (3)
As(1)–C(1)	1.943 (7)	1.939 (5)
As(1)–C(7)	1.927 (8)	1.931 (7)
As(1)–C(8)	1.928 (8)	1.930 (7)
As(2)–C(2)	1.943 (7)	1.943 (5)
As(2)–C(9)	1.935 (9)	1.918 (9)
As(2)–C(10)	1.924 (8)	1.939 (8)
C(1)–C(2)	1.382 (10)	1.391 (7)
C(2)–C(3)	1.401 (10)	1.383 (9)
C(3)–C(4)	1.351 (11)	1.377 (10)
C(4)–C(5)	1.387 (11)	1.372 (9)
C(5)–C(6)	1.401 (11)	1.383 (9)
C(6)–C(1)	1.384 (10)	1.390 (8)

[a] Standard deviations are given in parentheses.

is a $CH_3\cdots Cl^-$ ($C(7)\cdots Cl(2)$) distance of 3.46 Å, with a methyl hydrogen atom H(7′) directed very nearly along the $C\cdots Cl^-$ line. Two benzene carbon atoms, C(4) and C(6), are about 3.70 Å from the chloride ion, and again the hydrogen atoms H(4) and H(6) lie close to the $C\cdots Cl^-$ lines. A second methyl carbon atom, C(9), also lies about 3.70 Å from the chloride ion, but in this case the chloride ion lies approximately opposite the As–C bond and hence the hydrogen atoms are not involved.

The thermal ellipsoids for the nickel complex are represented in Figure 1. The patterns of anisotropy are very similar in the two compounds, although the $B(11)$ and $B(22)$ terms are systematically higher for the nickel compound. This difference does not seem to be due to our neglect of absorption corrections; the crystal of the nickel compound was the larger, particularly in the a and b directions, and we estimate that absorption effects should have decreased the apparent $B(11)$ terms by about 10%, relative to the cobalt compound, and the $B(22)$ terms by about 2%. We think it far more likely that the differences in the temperature factors represent differences in the characters of the two crystals. They have quite different morphologies; moreover, the larger extinction effects of the cobalt compound suggest a more "perfect" crystal that would be reflected in lower temperature factors.

TABLE IV
BOND ANGLES (DEG)[a]

	M = Ni	M = Co
As(1)–M–As(2)	86.8	86.6
As(1)–M–Cl(1)	92.5	91.8
As(2)–M–Cl(1)	93.3	92.4
C(1)–As(1)–M	107.6	107.9
C(7)–As(1)–M	117.0	116.8
C(8)–As(1)–M	119.7	120.2
C(1)–As(1)–C(7)	105.8	104.7
C(1)–As(1)–C(8)	101.0	101.2
C(7)–As(1)–C(8)	104.0	103.9
C(2)–As(2)–M	107.2	107.9
C(9)–As(2)–M	119.6	120.1
C(10)–As(2)–M	118.1	118.7
C(2)–As(2)–C(9)	102.5	101.7
C(2)–As(2)–C(10)	104.7	104.0
C(9)–As(2)–C(10)	102.9	102.1
As(1)–C(1)–C(2)	118.2	118.2
As(1)–C(1)–C(6)	121.4	122.2
As(2)–C(2)–C(1)	118.2	117.5
As(2)–C(2)–C(3)	122.3	122.9
C(1)–C(2)–C(3)	119.2	119.6
C(2)–C(3)–C(4)	120.4	121.0
C(3)–C(4)–C(5)	121.2	119.2
C(4)–C(5)–C(6)	118.9	121.0
C(5)–C(6)–C(1)	119.8	119.7
C(6)–C(1)–C(2)	120.4	119.4

[a] Standard deviations are about 0.5° for angles involving two or three carbon atoms, 0.3° for angles involving one carbon atom, and 0.05° for angles involving no carbon atoms.

Except for the position of the covalently bonded chlorine atom, there are no appreciable differences between the coordinates of corresponding atoms in the two compounds. The Ni–Cl distance is 2.425 (3) Å and the Co–Cl distance is 2.256 (3) Å. We attribute the elongation of the Ni–Cl bond to antibonding effects arising from the presence of an unpaired electron in the d_{z^2} orbital, which is empty in the cobalt compound. Our assumption that the unpaired electron is in the d_{z^2} orbital is based on a detailed analysis[12] of the single-crystal esr spectrum of $Ni(diars)_2Cl_2^+$.

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[12] P. K. Bernstein and H. B. Gray, *Inorg. Chem.*, **11**, 3035 (1972).