including that of $Re_2Br_6(PC_6H_5(C_2H_5)_2)_2$, currently under investigation in this laboratory.

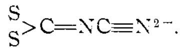
Table VI shows that the atoms Cl(1)–Cl(2)–Cl(3)–P form a plane with no deviations >0.1 Å and that the rhenium atom lies 0.62 Å out of this plane toward the other rhenium atom in the molecule. Also, the data of Table V show that the dihedral angle between planes 2 and 3 is 90.0°. Thus the symmetry of the $Cl_3PRe{-}ReCl_3P$ skeleton of the molecule is C_{2h} to a very good approximation.

Contribution from the Department of Chemistry, Massachusetts Institute of Technology,
Cambridge, Massachusetts 02139, and the Inorganic Materials Research Division of
Lawrence Radiation Laboratory and the Department of Chemistry,
University of California, Berkeley, California 94720

The Structure of Tetraphenylarsonium Bis(N-cyanodithiocarbimato)nickelate(II)[1]

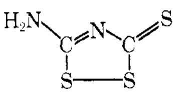
By F. A. Cotton and C. B. Harris

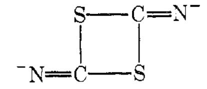
Received May 17, 1968

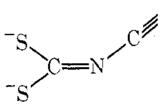
The crystal and molecular structures of tetraphenylarsonium bis(N-cyanodithiocarbimato)nickelate(II), $[(C_6H_5)_4As]_2[Ni(S_2CNCN)_2]$, have been determined by a single-crystal X-ray diffraction investigation. The substance crystallizes in the triclinic space group $A\bar{1}$ and has dimensions $a = 10.50 \pm 0.03$ Å, $b = 15.90 \pm 0.03$ Å, $c = 13.63 \pm 0.04$ Å, $\alpha = 90.02 \pm 0.05°$, $\beta = 101.74 \pm 0.07°$, and $\gamma = 89.51 \pm 0.07°$. The calculated and measured densities are: $\rho_{\text{calcd}} = 1.48$ g cm^{-3}; $\rho_{\text{measd}} = 1.51 \pm 0.04$ g cm^{-3} for $Z = 2$. The structure was refined by full-matrix least-square procedures to an R factor of 9.3% using 1671 statistically significant reflections collected by a θ–2θ scan technique on an automated diffractometer. The nickel atom is surrounded by a planar set of four sulfur atoms at an average distance of 2.188 Å. The transition metal complex has virtually C_{2h} point symmetry and its over-all structure confirms the conclusions previously put forward by Fackler and Coucouvanis and by Cotton and McCleverty as to the nature of the $C_2S_2N_2^{2-}$ ion and its metal complexes. It is, as proposed, the N-cyanodithiocarbimate ion,  $\overset{S}{\underset{S}{>}}C{=}NC{\equiv}N^{2-}$. Comparison of the present structure with that of bis(diethyldithiocarbamato)nickel(II) corroborates the prevailing view that there is appreciable double-bond character in the C—N bond in this and other complexes of dithiocarbamates.

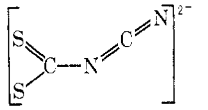
Introduction

Transition metal complexes of the N-cyanocarbimate ion, $[S_2C_2N_2]^{2-}$, have been prepared in several laboratories.[2,3] Fackler and Coucouvanis[3] have prepared and characterized transition metal complexes with the general class of 1,1-dithioanionic ligands, $S_2C{=}X^{2-}$. In particular, they prepared the N-cyanocarbimate ligand *via* the reaction of CS_2 with NCN^{2-}. In our laboratory[2] the N-cyanocarbimic acid and anion were prepared utilizing the reaction of xanthane hydride (I)[4,5] with base.[6] Originally[4] a cyclic structure (II) was proposed for the N-cyanocarbimate anion. Later, however, Hantzsch and Wolvekamp[7] proposed a noncyclic structure (III), mainly because such a structure appears more consistent with the formation of Cu(II), Pb(II), and Ag(I) complexes.[6] The observation[2,3b] of sharp strong bands in the infrared spectra of various complexes at ~2180 cm^{-1} supports structure III.


I


II


III


IV

Although the evidence just summarized is all indicative that a structure of type III is correct and that the S_2CNCN^{2-} ligand chelates through its two sulfur atoms, there has been no unequivocal proof of this. Furthermore, even if we assume that this type of structure is correct, it is of interest to know whether it is best represented by III, by IV, or by something intermediate.

A single-crystal X-ray diffraction study of a representative complex, $Ni(S_2CNCN)_2^{2-}$, in the form of its tetraphenylarsonium salt[3b] was therefore carried out. The results are reported here.

Procedure

Data Collection.—Crystals of tetraphenylarsonium bis(N-cyanodithiocarbimato)nickelate(II), $[(C_6H_5)_4As]_2[Ni(S_2CNCN)_2]$, were obtained by slow evaporation of a methanol solution. A well-formed crystal approximately 0.2 × 0.2 × 0.3 mm was mounted along the a^* axis. Systematic absences hkl for $k + l = 2n +$

---

[1] This work was supported by the National Science Foundation (Grant No. G. P. 7034X) and by Lawrence Radiation Laboratory, Inorganic Materials Research Division, under the auspices of the Atomic Energy Commission.

[2] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **6**, 229 (1967).

[3] (a) J. P. Fackler, Jr., and D. Coucouvanis, *Chem. Commun.*, 556 (1965); (b) J. P. Fackler, Jr., and D. Coucouvanis, *J. Am. Chem. Soc.*, **88**, 3913 (1966).

[4] W. v. Schneider and E. Erlenmeyer, *Ber.*, **3**, 339 (1870).

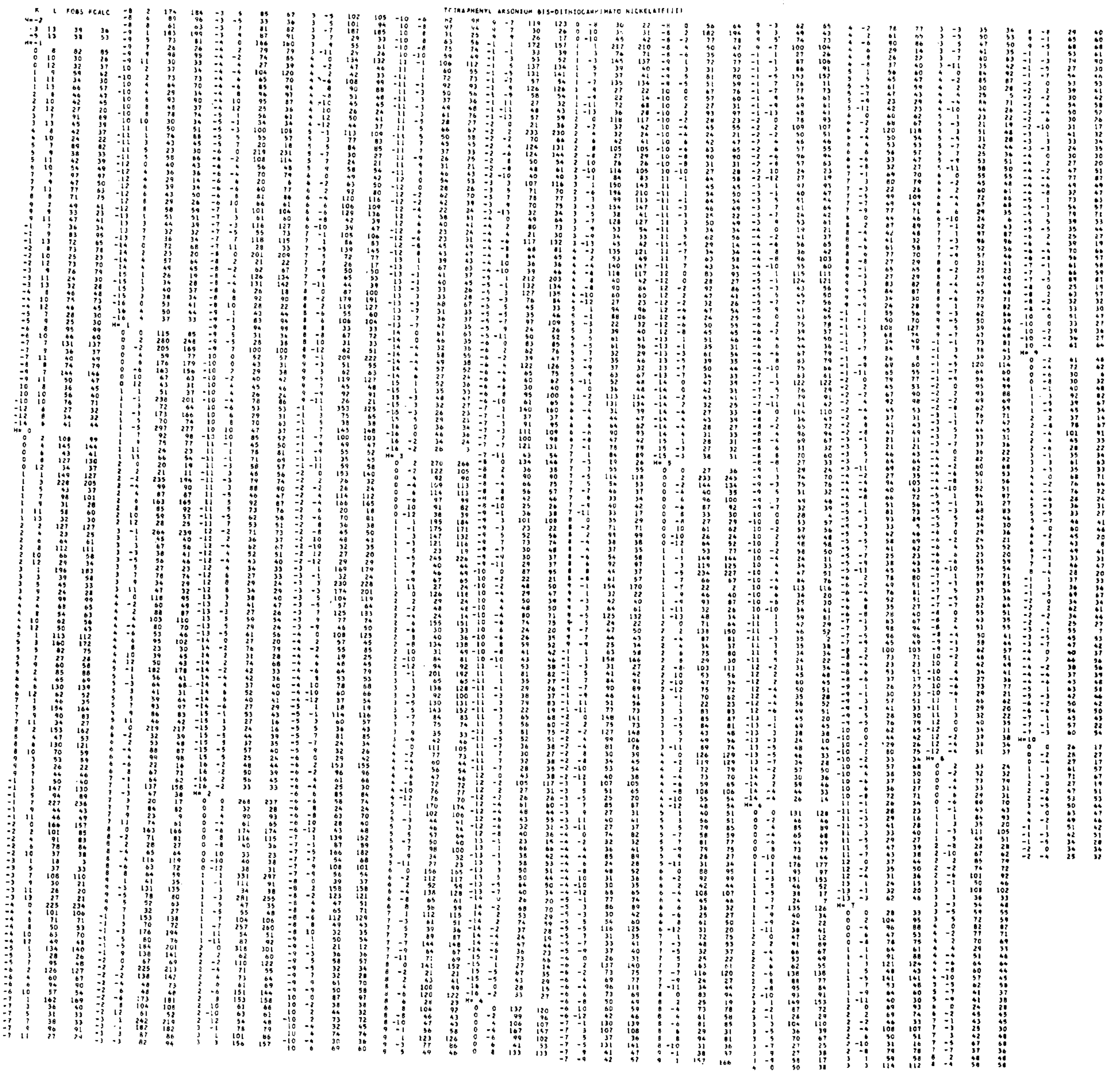
[5] A. Hordvik, *Acta Chem. Scand.*, **17**, 2575 (1963).

[6] A. Fleischer, *Ann.*, **179**, 204 (1875).

[7] A. Hantzsch and M. Wolvekamp, *ibid.*, **331**, 265 (1904).

TABLE I

OBSERVED AND CALCULATED STRUCTURE AMPLITUDES (SCALED TO $F(000) = 994$)



1 indicated the space group as A1 or A$\bar{1}$. Using a General Electric XRD-6 automated diffractometer with Mo Kα radiation ($\lambda(K\alpha_1)$ 0.70926 Å), the cell dimensions $a = 10.495 \pm 0.030$ Å, $b = 16.903 \pm 0.030$ Å, $c = 13.635 \pm 0.040$ Å, $\alpha = 90.02 \pm 0.05°$, $\beta = 101.74 \pm 0.07°$, and $\gamma = 89.51 \pm 0.07°$ were determined[8] at about 25°. The density, $\rho_{\text{measd}} = 1.51 \pm 0.04$ g cm^{-3}, measured by flotation compared satisfactorily with a calculated value $\rho_{\text{calcd}} = 1.48$ g cm^{-3} assuming two molecules per unit cell.

Using Zr-filtered Mo Kα radiation 2470 independent reflections were collected by a θ–2θ scanning technique. Using a 4° takeoff angle, each peak was scanned from $2\theta_{\text{calcd}} - 1.33°$ to $2\theta_{\text{calcd}} + 1.33°$ in 40 sec while background was counted for 20 sec on each side of the peak. Of these reflections 1671 were accepted as statistically above background ($\sigma < 0.5$ and $\sigma = (\text{peak} + \text{background})^{1/2}/(\text{peak} - \text{background})$). These data were corrected for Lorentz and polarization factors. The morphology of the crystal was determined by optical techniques and transmission factors (0.62–0.74) were calculated[9] for each reflection using a linear absorption coefficient $\mu = 20.7$ cm^{-1}. The resulting data were used as input for computing the Patterson function.

Solution and Refinement of the Structure.—From a three-dimensional Patterson function[10] the positions of the nickel atom, both arsenic atoms, and the four sulfur atoms were determined. The Patterson function could only account for the above atoms in the space group A$\bar{1}$ with the nickel at the origin of the unit cell. It seemed safe to assume A$\bar{1}$ as the correct space

---

[8] The uncertainty given represents the precision of the diffractometer data points used to calculate the cell constants. The reduced, primative unit cell (P$\bar{1}$) has the following dimensions: $a = 10.495$ Å; $b = 10.859$ Å; $c = 15.421$ Å; $\alpha = 118.21°$; $\beta = 120.05°$; $\gamma = 96.95°$.

[9] W. C. Hamilton, "Goniostat Polyhehral Absorption and Extinction Correction Program for the IBM 7094," 1960.

[10] W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende, "A Two- and Three-Dimensional Fourier Program for the IBM 709/7090, ERFR-2," 1962.

group, since only the phenyl rings on different arsenic atoms could reduce the symmetry to A1. The subsequent successful refinement confirmed the choice of A$\bar{1}$.

Using nickel, arsenic, and two sulfur atoms (all other atoms of these kinds are related by symmetry), the signs of the observed structure amplitudes were calculated[11] and used in synthesizing[12] a three-dimensional Fourier map employing the atomic scattering factors of Ibers[13a] corrected for the real and imaginary components of anomalous dispersion.[13b] All other atoms in the structure were then found.

Reasonable isotropic temperature factors were assigned to all atoms, and two cycles of least-squares refinement[11] of the over-all scale factor and the positional coordinates of all atoms except Ni at (0, 0, 0) were carried out minimizing $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weights, w, were all taken as unity. At this point the residual, R_2, was 0.386. Four cycles of least-squares refinement of the isotropic temperature factors, positional parameters, and over-all scale factor reduced R_2 to 0.116. The structure could be considered refined to its isotropic limit. The isotropic temperature factors for all atoms, however, were uniformly high.

Anisotropic temperature factors of the form $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$ were introduced for all atoms except the 24 phenyl carbon atoms. Table III records values of $B_{ij} = 4\beta_{ij}/a^*_ia^*_j$, where a^*_i is the length of the ith reciprocal axis. Six cycles of least-squares refinement of all parameters reduced the (unit weighted) R_2 to 0.094. There were no anomalous isotropic or anisotropic temperature factors, though both were still somewhat high.

A weighting scheme based on the Cruickshank criterion[14] that $w\Delta^2$ be constant for all ranges of data was devised as follows: for $|F_o| \leq 166$, $\sigma = (0.211|F_o| + 50)^{1/2}$; for $|F_o| > 166$, $\sigma = (4.08|F_o| - 593)^{1/2}$. Four cycles of least-squares refinement of all parameters caused no significant shift in the parameters but caused a 10–15% decrease in the estimated standard deviations.

A final difference Fourier map revealed no disorder and no peaks greater than 1.5 e$^-$/Å^3. The average peak height of a carbon atom on the last electron density map was 5.5 e$^-$/Å^3. At this point the unit weighted R_2 had converged to a final value of 0.093. The weighted R_2 was not calculated by the least-squares program used.

Results

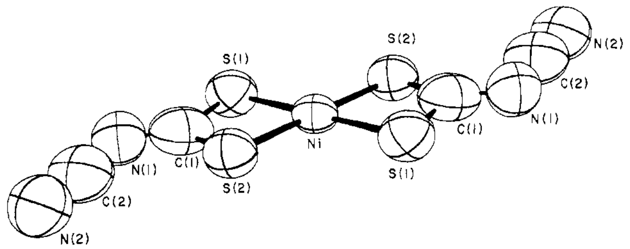


Figure 1.—The complex anion $Ni(S_2CNCN)_2^{2-}$. The atoms are represented by their thermal vibration elipsoids.

Perspective views[15] of the complex anion and the tetraphenylarsonium cation are shown in Figures 1 and 2, respectively. Each atom is represented by the ellipsoid of its thermal vibration tensor.

Table I lists the calculated structure factors and the observed structure amplitudes. The positional parameters and isotropic temperature factors are listed in Table II while the anisotropic temperature factors are tabulated in Table III.

Table II

Fractional Coordinates and Isotropic Temperature Factors for Atoms in the Asymmetric Unit[a]

Atom	x	y	z	B
Ni	0.0	0.0	0.0	. . .
S(1)	0.0495 (6)	0.9856 (3)	0.8529 (4)	. . .
S(2)	0.0154 (6)	0.8709 (4)	0.9921 (4)	. . .
C(1)	0.0587 (17)	0.8871 (13)	0.8767 (18)	. . .
N(1)	0.0893 (17)	0.3282 (11)	0.3257 (14)	. . .
C(2)	0.1276 (22)	0.3477 (15)	0.2414 (19)	. . .
N(2)	0.1628 (20)	0.3566 (13)	0.1662 (16)	. . .
As	0.4773 (2)	0.4318 (1)	0.7709 (1)	. . .
C(11)	0.3399 (18)	0.3735 (11)	0.8058 (14)	9.6 (4)
C(12)	0.3100 (23)	0.3893 (13)	0.8966 (17)	11.8 (5)
C(13)	0.2073 (23)	0.3446 (14)	0.9288 (17)	11.7 (5)
C(14)	0.1507 (23)	0.2858 (14)	0.8639 (18)	12.0 (6)
C(15)	0.1819 (23)	0.2711 (14)	0.7729 (18)	11.9 (5)
C(16)	0.2778 (21)	0.3149 (12)	0.7421 (16)	10.9 (5)
C(21)	0.4901 (19)	0.4087 (11)	0.6381 (14)	9.5 (4)
C(22)	0.3826 (19)	0.4260 (12)	0.5587 (15)	10.3 (4)
C(23)	0.3915 (22)	0.4090 (13)	0.4612 (16)	11.2 (5)
C(24)	0.5053 (22)	0.3765 (13)	0.4432 (17)	11.2 (5)
C(25)	0.6174 (22)	0.3619 (13)	0.5188 (17)	11.4 (5)
C(26)	0.6044 (21)	0.3788 (12)	0.6185 (16)	10.9 (5)
C(31)	0.6361 (20)	0.4042 (12)	0.8577 (15)	10.4 (5)
C(32)	0.6428 (21)	0.3438 (13)	0.9244 (17)	11.2 (5)
C(33)	0.7677 (26)	0.3212 (15)	0.9860 (19)	12.7 (6)
C(34)	0.8743 (25)	0.3635 (15)	0.9791 (19)	12.5 (6)
C(35)	0.8710 (23)	0.4228 (14)	0.9118 (18)	11.6 (5)
C(36)	0.7516 (23)	0.4446 (14)	0.8476 (17)	11.7 (5)
C(41)	0.4368 (18)	0.5376 (11)	0.7870 (14)	9.6 (4)
C(42)	0.5277 (20)	0.5908 (12)	0.8344 (15)	10.3 (4)
C(43)	0.4936 (22)	0.6696 (13)	0.8420 (17)	11.6 (5)
C(44)	0.3710 (22)	0.6983 (13)	0.8045 (16)	11.1 (5)
C(45)	0.2765 (22)	0.6446 (13)	0.7569 (16)	11.3 (5)
C(46)	0.3063 (20)	0.5654 (12)	0.7476 (15)	10.8 (5)

[a] Figures in parentheses are estimated standard deviations occurring in the last significant figure.

Table IV lists all salient bond distances and bond angles according to the numbering schemes of Figures 1 and 2.

Discussion

The structure of the $Ni(S_2CNCN)_2^{2-}$ ion shows that the dithiocarbimate ion does, as the name was chosen[3] to suggest, have a structure of the type III (or IV).

---

[11] A. Zalkin, modification of "Ganzel–Sparks–Trueblood Full-Matrix Least-Squares Program for the CDC 6600, LS200," unpublished. This program minimizes the function $\Sigma w(|F_o| - |F_c|)^2$.

[12] A. Zalkin, "Fourier Data Processing Program for the CDC 6600, FODAP," unpublished.

[13] (a) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, The Kynoch Press, Birmingham, England, 1962, p 202; (b) J. A. Ibers, *ibid.*, p 216.

[14] D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press Inc., New York, N. Y., 1965, p 113.

[15] C. K. Johnson, "A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations, ORTEP," 1965.

TABLE III

ANISOTROPIC TEMPERATURE FACTORS[a] IN Å²

Atom	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
As	4.86 (9)	6.32 (11)	4.87 (9)	−0.67 (7)	0.53 (7)	0.46 (7)
Ni	5.42 (17)	6.55 (19)	5.90 (18)	−0.50 (14)	1.36 (14)	0.75 (15)
S(1)	8.22 (30)	8.65 (31)	7.79 (28)	−0.69 (24)	2.26 (23)	0.90 (24)
S(2)	9.01 (34)	8.73 (32)	8.58 (31)	−1.23 (26)	2.73 (26)	1.00 (25)
C(1)	7.3 (9)	10.9 (12)	13.3 (14)	0.1 (8)	1.3 (9)	1.8 (11)
N(1)	10.2 (10)	9.9 (10)	10.3 (10)	−0.5 (8)	2.6 (8)	−0.28 (8)
C(2)	10.0 (12)	14.4 (17)	9.6 (12)	−0.6 (11)	0.8 (10)	1.3 (12)
N(2)	11.3 (12)	14.3 (14)	10.2 (11)	−0.4 (10)	1.6 (9)	−0.2 (10)

[a] Figures in parentheses are estimated standard deviations occurring in the last significant figure.

TABLE IV

BOND DISTANCES AND BOND ANGLES[a]

A. Bond Distances, Å

Ni–S(1)	2.185 (8)	C(2)–N(2)	1.17 (3)
Ni–S(2)	2.192 (7)	As–C(11)	1.89 (2)
S(1)–C(1)	1.69 (2)	As–C(21)	1.88 (2)
S(2)–C(1)	1.75 (3)	As–C(31)	1.89 (2)
C(1)–N(1)	1.29 (3)	As–O(41)	1.86 (2)
N(1)–C(2)	1.34 (3)		

Ring, *n*	C(*n*1)– C(*n*2)	C(*n*2)– C(*n*3)	C(*n*3)– C(*n*4)	C(*n*4)– C(*n*5)	C(*n*5)- C(*n*6)	C(*n*6)– C(*n*1)
1	1.36 (3)	1.46 (3)	1.39 (3)	1.37 (3)	1.39 (3)	1.39 (3)
2	1.42 (3)	1.38 (3)	1.38 (3)	1.42 (3)	1.42 (3)	1.37 (3)
3	1.36 (3)	1.45 (3)	1.35 (4)	1.36 (3)	1.42 (3)	1.43 (3)
4	1.38 (3)	1.39 (3)	1.37 (3)	1.41 (3)	1.38 (3)	1.44 (3)
Av	1.38	1.42	1.37	1.39	1.40	1.41

B. Bond Angles, Deg

S(1)–Ni–S(2)	79.2 (2)	C(1)–N(1)–C(2)	115 (2)
Ni–S(1)–C(1)	86.9 (8)	N(1)–C(2)–N(2)	173 (3)
Ni–S(2)–C(1)	85.5 (8)	C(11)–As–C(21)	110 (1)
S(1)–C(1)–S(2)	108 (1)	C(11)–As–C(31)	110 (1)
Ni–C(1)–N(1)	174 (2)	C(11)–As–C(41)	106 (1)
S(1)–C(1)–N(1)	132 (2)	C(21)–As–C(31)	109 (1)
S(2)–C(1)–N(1)	120 (2)	C(21)–As–C(41)	112 (1)
		C(31)–As–C(41)	111 (1)

Ring, *n*	C(*n*1)– C(*n*2)– C(*n*3)	C(*n*2)– C(*n*3)– C(*n*4)	C(*n*3)– C(*n*4)– C(*n*5)	C(*n*4)– C(*n*5)– C(*n*6)	C(*n*5)– C(*n*6)– C(*n*1)	C(*n*6)– C(*n*1)– C(*n*2)
1	120 (2)	116 (2)	124 (2)	120 (2)	118 (2)	123 (2)
2	120 (2)	119 (2)	124 (2)	116 (2)	121 (2)	121 (2)
3	120 (2)	119 (2)	122 (2)	120 (2)	119 (2)	120 (2)
4	120 (2)	123 (2)	118 (2)	121 (2)	119 (2)	119 (2)
Av	120	119	122	119	119	121

Ring, *n*	As– C(*n*1)– C(*n*2)	As– C(*n*1)– C(*n*6)	As– C(*n*1)– C(*n*4)
1	117 (2)	120 (2)	177 (1)
2	119 (1)	120 (2)	179 (1)
3	121 (2)	119 (2)	178 (1)
4	122 (2)	119 (1)	178 (1)
Av	120	120	178

[a] Figures in parentheses are estimated standard deviations occurring in the last significant figure.

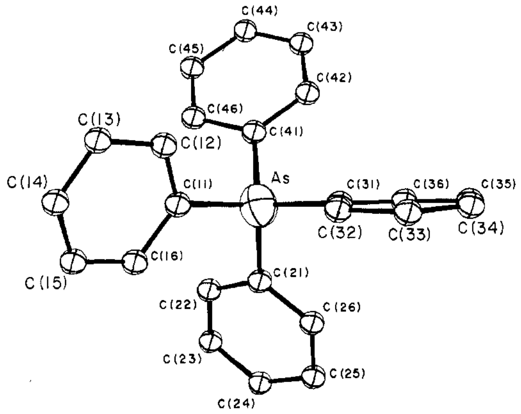


Figure 2.—The $(C_6H_5)_4As^+$ ion.

The detailed dimensions[16] can be accounted for by assuming that III fairly well describes the electron distribution.

The C(1)–N(1)–C(2) and N(1)–C(2)–N(2) angles, 115 (2) and 173 (3)°, respectively, are equally consistent with III or IV, but the C(1)–N(1), N(1)–C(2), and C(2)–N(2) distances, 1.29, 1.34, and 1.17 Å, respectively, clearly favor the predominance of III. In particular, the "cyano" C(2)–N(2) distance, 1.17 (3) Å, is close to the typical value, 1.16 Å, for $C{\equiv}N$, whereas for $C{=}N$ a considerably longer bond, ~1.35 Å, would be expected.[17]

The NiS_4 group is rigorously planar owing to the fact that the Ni atom lies at a crystallographic center of symmetry.

It is of particular interest to compare the $Ni(S_2CNCN)_2{}^{2-}$ ion with the N,N-diethyldithiocarbamate complex of nickel, $Ni[S_2CN(C_2H_5)_2]_2$, the structure of which has recently been described.[18] There are no significant differences between any of the corresponding distances or angles in the central $Ni(S_2CN)_2$ portions of the two molecules. Thus, if the dithiocarbimate ion in its complex is best represented by III as compared to IV, then it follows that, as Chatt, Duncanson, and Venanzi[19] first proposed on the basis of infrared evidence, the electronic structures of $M(S_2CNR_2)_2$ complexes are indeed described by a hybrid of V and VI in which V greatly predominates. There is structural evidence to show that the copper[20] and zinc[21] dithiocarbamates closely resemble $Ni[S_2CN(C_2H_5)_2]_2$, while with xanthates the canonical form corresponding to VI seems to predominate.[22]

---

(16) Because of the standard deviations of 0.03 Å in the C–N distances and 2–3° in the angles at such atoms, together with the fact that no corrections have been made for the effect of the rather large amplitudes of the thermal vibrations, restraint must be exercised in discussing the finer implications of the dimensions.

(17) Typical bond lengths or bond lengths in other compounds cited without explicit reference are from L. E. Sutton, Ed., "Tables of Interatomic Distances and Configuration in Molecules and Ions" and "Interatomic Distances Supplement," Special Publications No. 11 and 18, The Chemical Society, London, 1958 and 1965.

(18) M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, **19**, 619 (1965).

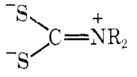
(19) J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Nature*, **177**, 1042 (1956); *Suomen Kemistilehti*, **B29**, 75 (1956).

(20) M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and M. Zambonelli, *Acta Cryst.*, **19**, 886 (1965).

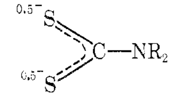
(21) M. Bonamico, G. Mazzone, A. Vaciago, and L. Zambonelli, *ibid.*, **19**, 898 (1965).

(22) M. Franzini, *Z. Krist.*, **118**, 393 (1963).

The bond distances and angles in the $(C_6H_5)_4As^+$ ion are all close to the normal, accepted values.[17] However, the angles of rotation of the four phenyl groups about their respective As–C(*n*1)–C(*n*4) axes are such that the $(C_6H_5)_4As^+$ ion does not approximate to any symmetrical conformation (such as D_{2d} or S_4). In some other cases such high symmetries have been found[23,24] although more or less drastic departures from symmetry seem to be common.[25,26] It is precisely this flexibility which makes $(C_6H_5)_4As^+$ such a useful cation for obtaining crystalline salts of large, irregularly shaped anions.



V



VI

---

(23) R. C. L. Mooney, *J. Am. Chem. Soc.*, **62**, 2995 (1940).

(24) B. Zaslow and R. E. Rundle, *J. Phys. Chem.*, **61**, 490 (1957).

(25) F. A. Cotton and S. J. Lippard, *Inorg. Chem.*, **5**, 416 (1966).

(26) J. G. Bergman, Jr., and F. A. Cotton, *ibid.*, **5**, 1420 (1966).

Contribution from the Physics and Chemistry Departments,
Duquesne University, Pittsburgh, Pennsylvania 15219

The Crystal and Molecular Structure of Bis(pyridine-2-carboxamido)nickel(II) Dihydrate[1]

By SHIH C. CHANG, DONG Y. PARK, and NORMAN C. LI

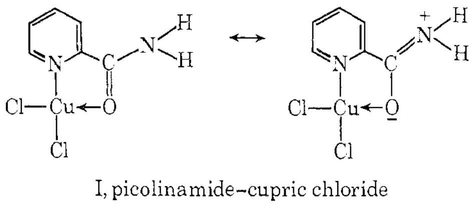
Received January 22, 1968

The crystal and molecular structure of bis(pyridine-2-carboxamido)nickel(II) dihydrate, $Ni(C_6H_5N_2O)_2 \cdot 2H_2O$, isolated from aqueous solution of pH 11.5, has been determined from three-dimensional X-ray data collected by the multiple-film Weissenberg method. The unit cell dimensions are: $a = 7.63 \pm 0.02$ Å, $b = 4.49 \pm 0.01$ Å, $c = 12.45 \pm 0.06$ Å, $\beta = 90.0 \pm 0.3°$. The crystal is a twinned composite with monoclinic components. The space group is $P2_1/c$, $Z = 2$, and the measured and calculated densities are 1.59 and 1.56 g cm^{-3}, respectively. The intensity data show essentially the orthorhombic mmm symmetry due to microscopic twinning. By using an incoherent twinning model, the structure was solved and refined by a least-squares method. Without the hydrogens, the final *R* factor is 10.7% for the 840 reflections. The pyridine ring nitrogen and the amide nitrogen are bonded to nickel with bond lengths of 1.92 and 1.87 (±0.01) Å, respectively. The four nitrogens of the two ligands bonded to nickel form a planar structure in *trans* configuration, and the water molecules are not coordinated to nickel. The molecules form infinite zigzag layers perpendicular to the *b* axis. The layers are held together by the hydrogen bonds of the waters of hydration and the van der Waals forces between the molecules. The twinning factor observed (*m*) is 0.56. It may be that a layer of the reversed structure stacks on one constituent structure component thus causing the twinning phenomenon.

Introduction

Crystal and molecular structures of amino acids, peptides, and acid amides have been investigated in detail by several authors because of their biological importance. Recently Conley and Martin[2] reported that picolinamide (pyridine-2-carboxamide), a derivative of an α-amino acid, forms different complexes with Cu^{2+} or Ni^{2+} in aqueous solution at different pH values and found that titration of solutions containing 2 mol of picolinamide per mol of Cu^{2+} or Ni^{2+} requires the addition of 2 equiv of base per mol of metal ion to reach pH 10. The original blue picolinamide–cupric and picolinamide–nickel ion solutions at the beginning of the titration change color to violet and to yellow-orange, respectively, during the course of the titration, and these color changes are typical of those found in peptides where amide hydrogens undergo cupric[3] or nickel[4] ion promoted ionizations. Conley and Martin[2] suggested that cupric or nickel ion promotes the ionization of two amide hydrogens forming at high pH a 2:1 ligand–metal complex with the ligands chelated through nitrogen atoms. Conley and Martin[2] also described the preparation of a neutral bis(pyridine-2-carboxamido)nickel(II) complex yielding red needles.

Nagano, *et al.*,[5] reported the isolation in the solid state of a 1:1 $CuCl_2$ complex of picolinamide and suggested that the structure of the complex is



I, picolinamide–cupric chloride

Their suggestion was based solely on the directions of shift of the infrared bands of the C=O and C—N stretching vibrations and the ring vibrations. Since, at the time this research was undertaken, the crystal and molecular structure of metal complexes of picolin-

---

(1) Research sponsored by the National Science Foundation, Grant No. GB-4065. Material to be presented by D. Y. Park to the Graduate School of Duquesne University as part of his Ph.D. thesis in the Chemistry Department.

(2) H. L. Conley, Jr., and R. B. Martin, *J. Phys. Chem.*, **69**, 2914 (1965).

(3) W. L. Koltun, R. H. Roth, and F. R. N. Gurd, *J. Biol. Chem.*, **238**, 124 (1963); W. L. Koltun, M. Fried, and F. R. N. Gurd, *J. Am. Chem. Soc.*, **82**, 233 (1960).

(4) R. B. Martin, M. Chamberlin, and J. T. Edsall, *ibid.*, **82**, 495 (1960); R. B. Martin and J. T. Edsall, *ibid.*, **82**, 1107 (1960).

(5) K. Nagano, H. Kinoshita, and A. Hirakawa, *Chem. Pharm. Bull.* (Tokyo), **12**, 1198 (1964).