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Authors

Cotton, F.A.
Harris, C.B.

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University of California

Ernest O. Lawrence
Radiation Laboratory

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

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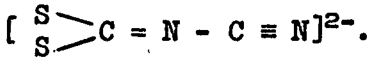
ABSTRACT

The crystal and molecular structures of tetraphenylarsonium bis-(N-cyanodithiocarbimato)nickelate(II) 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 $a = 10.50$ Å, $b = 16.90$ Å, $c = 13.63$ Å, $\alpha = 90.02^\circ$, $\beta = 101.74^\circ$, and $\gamma = 89.51^\circ$. The calculated and measured densities are: $\rho_{calc} = 1.48$ g. cm^{-3}; $\rho_{meas} = 1.51 \pm 0.04$ 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 $\theta/2\theta$ 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 overall 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,  $[{}^{S}_{S}{>}C = N - C \equiv N]^{2-}$. Comparison of the present structure with that of bis-(diethyldithiocarbamato)nickel(II) corrorborates 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

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

(3) (a) J. P. Fackler, Jr. and D. Coucouvanis, Chem. Comm., 556 (1965).
(b) J. P. Fackler, Jr. and D. Coucouvanis, J. Am. Chem. Soc., 88, 3913 (1966).

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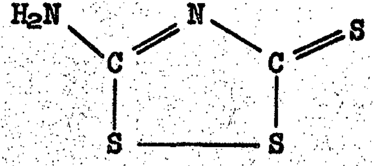
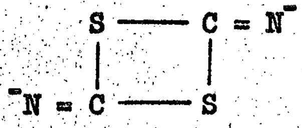
(4) W. v. Schneider and E. Erlenmeyer, *Ber.*, **3**, 339 (1870).

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

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



(I)



(II)

structure (II) was proposed for the N-cyanocarbimate anion. Later, however, Hantzsch and Wolvekamp[7] proposed a non-cyclic structure (III), mainly because

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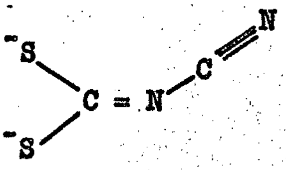
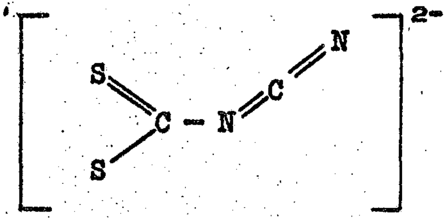
(7) A. Hantzsch and M. Wolvekamp, *ibid.*, **331**, 265 (1904).



(III)



(IV)

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.

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

<u>Data Collection</u>. - Crystals of tetraphenylarsonium bis-(N-cyanodithiocarbimato)nickelate(II), $(\phi_4As)_2Ni(S_2CNCN)_2$, were obtained by slow evaporation of a methanol solution. A well-formed crystal approximately 0.2 x 0.2 x 0.3 mm was mounted along the a* axis. Systematic absences $hk\ell$ for $k + \ell = 2n + 1$ indicated the space group as A1 or $A\bar{1}$. Using a General Electric XRD-6 automated diffractometer with Mo $K\alpha$ radiation ($\lambda K_{\alpha_1} = 0.70926$), 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]

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(8) The uncertainty given represents the precision of the diffractometer data points used to calculate the cell constants.

at about 25°C. The density, $\rho_{meas} = 1.51 \pm 0.04$ g. cm^{-3}, measured by flotation compares satisfactorily with a calculated value $\rho_{calc} = 1.48$ g. cm^{-3} assuming two molecules per unit cell.

Using Zr filtered Mo Kα radiation 2470 independent reflections were collected by a $\theta/2\theta$ scanning technique. Using a 4° take-off angle, 2.66° was scanned in 40 seconds while background was counted for 20 seconds 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 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 group, since only the phenyl rings on different arsenic atoms could reduce the symmetry to $A1$. The subsequent successful refinement confirmed the choice of $A\bar{1}$.

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(9) C. W. Burnham, "Computing Transmission Factors of Crystals of Essentially Arbitrary Shape for the IBM 709/7090 (GNABS).

(10) W. G. Sly, D. P. Shoemaker and J. H. Van den Hende, "A Two- and Three-Dimensional Fourier Program for the I.B.M. 709/7090 (ERFR-2), (1962).

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 overall scale factor and the positional coordinates of all atoms except Ni at (0,0,0) was carried out minimizing $R_2 = [\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$. $|F_o|$ and $|F_c|$ are the observed and calculated structure amplitudes, and the weights, ω, were all taken as unity. At this point the residual, R_2, was 0.386. Four cycles

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

(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, Kynoch Press, Birmingham, England, 1962, p. 202.

(b) *Ibid.*, page 216.

of least squares refinement of the isotropic temperature factors, positional parameters and overall 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 $\exp-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}\ell^2 + 2\beta_{12}hk + 2\beta_{13}h\ell + 2\beta_{23}k\ell)$ were introduced for all atoms except the 24 phenyl carbon atoms. Table III records values of $B_{ij} = 4\beta_{ij}/a^*_i a^*_j$, 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 $\omega\Delta^2$ 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/$\mathring{A}^3$. 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.

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(14) D. W. J. Cruickshank in "Computing Methods in Crystallography," J. S. Rollett, Ed., Pergamon Press, New York, p. 113 (1965).

RESULTS

Stereographic plots[15] of the complex anion and the tetraphenylarsonium cation are shown in Figs. 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 IV lists all salient bond distances and bond angles according to the numbering schemes of Figs. 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). The detailed dimensions[16] can be accounted for by assuming

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

(16) Because of the standard deviations of 0.03 Å in the C to 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.

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]

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

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(17) Typical bond lengths or bond lengths in other compounds cited without explicit reference are from "Tables of Interatomic Distances and Configuration in Molecules and Ions" and "Interatomic Distances Supplement," L. E. Sutton, Ed., Special Publications Nos. 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).

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]

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-Ci1-Ci4 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]

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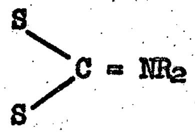
(19) J. Chatt, L. A. Duncanson and L. M. Venanzi, *Nature*, **177**, 1042 (1956); *idem.*, *Suomen Kem.*, **B29**, 75 (1956).

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

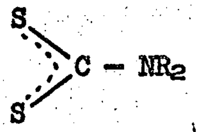
(21) M. Bonamico, G. Mazzone, A. Vaciago and L. Zambonelli, *ibid.*, **19**, 898 (1965).

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

although more or less drastic departures from symmetry seem to be common.[25,26] It is precisely this flexibility which makes the $(C_6H_5)_4As^+$ such a useful cation for obtaining crystalline salts of large, irregularly shaped anions.



V



VI

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(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).

TABLE I

Observed and Calculated Structure Amplitudes

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)

TABLE II (continued)

Atom	x	y	z	B
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 III

Anisotropic Temperature Factors[a] in $\mathring{A}^2$

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 in Å

Ni-S(1)	2.185(8)	C(2)-N(2)	1.17(3)
Ni-S(2)	2.192(7)	As-C11	1.89(2)
S(1)-C(1)	1.69(2)	As-C21	1.88(2)
S(2)-C(1)	1.75(3)	As-C31	1.89(2)
C(1)-N(1)	1.29(3)	As-C41	1.86(2)
N(1)-C(2)	1.34(3)		

Ring,n	C(n1)-C(n2)	C(n2)-C(n3)	C(n3)-C(n4)	C(n4)-C(n5)	C(n5)-C(n6)	C(n6)-C(n1)
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)
Ave.	1.38	1.42	1.37	1.39	1.40	1.41

(a) Figures parentheses are estimated standard deviations occurring in the last significant figure.

TABLE IV (continued)

B. Bond Angles in Degrees

S(1)- Ni -S(1)	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)	C11- As -C21	110(1)
S(1)-C(1)-S(2)	108(1)	C11- As -C31	110(1)
Ni-C(1)-N(1)	174(2)	C11- As -C41	106(1)
S(1)-C(1)-N(1)	132(2)	C21- As -C31	109(1)
S(2)-C(1)-N(1)	120(2)	C21- As -C41	112(1)
		C31- As -C41	111(1)

Ring,n	C(n1)-C(n2)-C(n3)	C(n2)-C(n3)-C(n4)	C(n3)-C(n4)-C(n5)	C(n4)-C(n5)-C(n6)	C(n5)-C(n6)-C(n1)	C(n6)-C(n1)-C(n2)
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)
ave.	120	119	122	119	119	121

Ring,n	As-C(n1)-C(n2)	As-C(n1)-C(n6)	As-C(n1)-C(n4)
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)
ave.	120	120	178

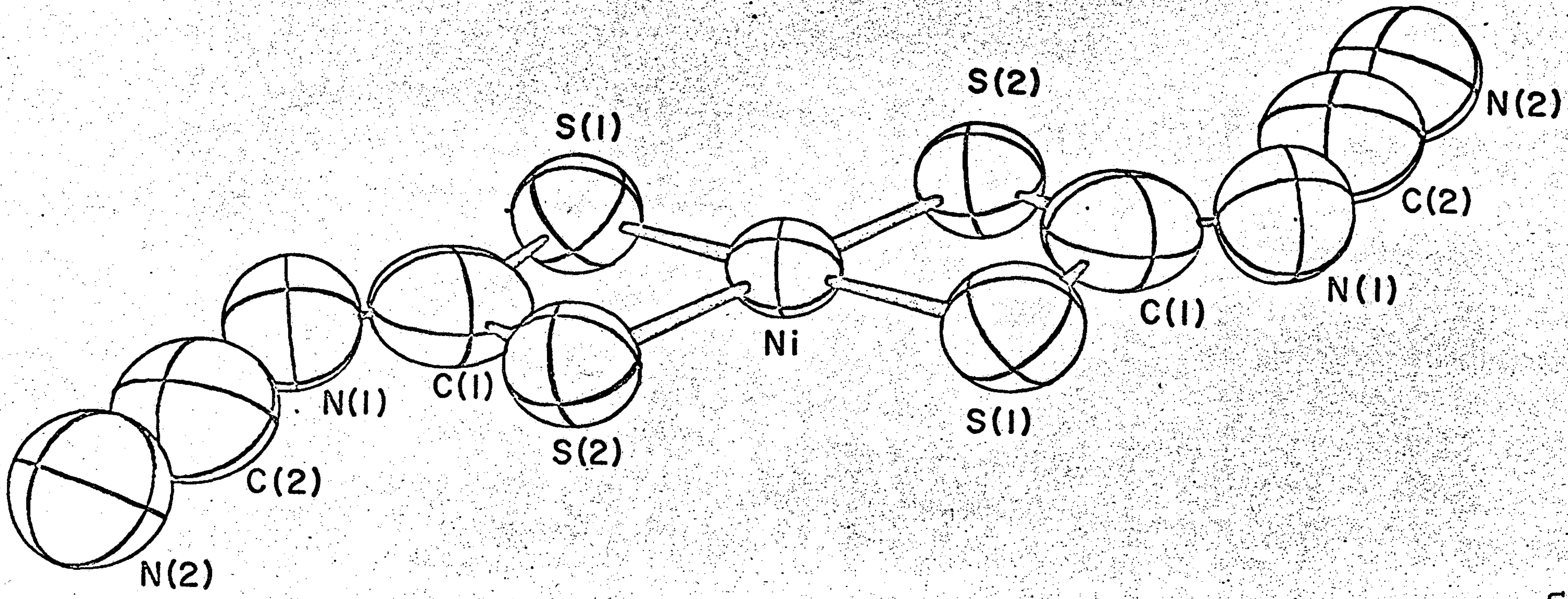

Figure 1. The complex anion $[Ni(S_2CNCN)_2]^{2-}$. The atoms are represented by their thermal vibration ellipsoids.

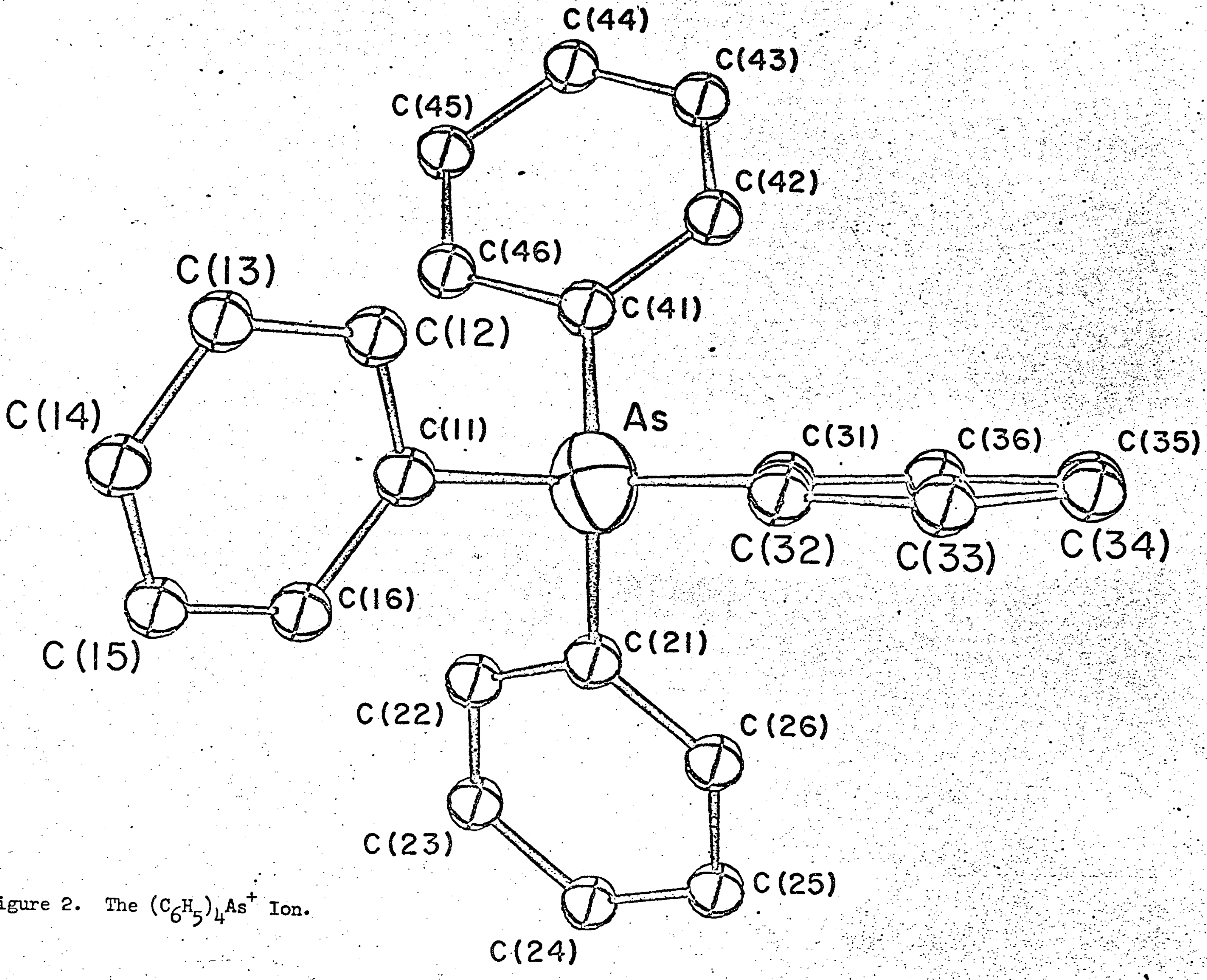

Figure 2. The $(C_6H_5)_4As^+$ Ion.