

shown by Jensen and Dahl,⁵ trimethylphosphine forms Ni(II) complexes which differ in composition from those formed by triethylphosphine and higher aliphatic phosphines. *A priori*, therefore, the same structures for the trimethylphosphine and the triethylphosphine silver iodide complexes can not be assumed. The molecular weight of the trimethylphosphine complex was determined cryoscopically in benzene. The agreement between the measured molecular weight (Table 2) and the calculated molecular weight for a tetrameric compound is satisfactory, as the uncertainty in the measured values is approximately 10 % because of the rather low solubility in benzene. Several other solvents (acetophenone, bromoform, ethylene bromide) were tried, but in cases where the compound was more soluble than in benzene, extensive decomposition or dissociation occurred.

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Note on the Crystal Structure of $\text{Cu}(\text{N}_3)_2$

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Recently the crystal structure of $\text{Cu}(\text{N}_3)_2$ has been determined,^{1,2} by means of single crystal X-ray methods. The structure can be visualized as being built up of almost

planar chain molecules, running parallel to the *b*-axis. These chains are coupled to form double chains, which in their turn are joined together by azide groups lying in planes perpendicular to the *b*-axis. Although the two investigations gave identical pictures of the structure within the limits of experimental error, we thought it worth while to combine the intensity data from both determinations and to refine the structure further, in the hopes that still more accurate atomic parameters might be obtained.

In order to be able to compare the two sets of data, they were first refined separately on the same computer. The magnitudes of the temperature factors computed were, however, found to differ for the two reflexion materials, which meant that there were discrepancies especially between reflexions with high $\sin \theta$ -values. In order to make the two sets of data comparable, the ratio between the structure factors for the same reflexion in the two reflexion materials was plotted as a function of $\sin \theta/\lambda$. This plot was used to obtain the reflexions which were present in only one of the two reflexion materials on the same basis as the average value of the observed structure factors for the reflexions present in both sets of data. The reflexions which were present in only one reflexion material (R.S.) were among the weakest ones.

The final refinement, based on the combined reflexion material, was performed in two different ways:

A. All reflexions were given equal weight and the refinement was based on 408 observed independent reflexions. The *R*-value obtained was 0.062 and the standard deviations were a little lower than for the original sets of data.

B. The average values of the reflexions observed in both reflexion materials were given double weight compared with those observed in only one of the reflexion materials. This was achieved by giving the computer the average values twice and the single values once. The *R*-value thus obtained was 0.055.

In both cases all atoms were refined anisotropically. There was no statistical difference between the atomic positions determined by the two different methods, although method B might be supposed to yield the more accurate parameters. The results given in the tables are therefore those of method B. Since the standard deviations must, however, be based on the independent reflexions, the values of the

Table 1. Atomic coordinates (expressed as fractions of the cell edges) with their standard deviations and thermal parameters for $\text{Cu}(\text{N}_3)_2$. Anisotropic temperature factors are of the form $\exp[-(h^2B_{11} + k^2B_{22} + l^2B_{33} + 2hlB_{13})]$, and isotropic temperature factors of the form $\exp[-B(\sin^2\theta/\lambda^2)]$. I denotes the combined determination, II² and III¹ the original determinations.

	<i>x</i>	<i>y</i>	<i>z</i>	B_{11} or B	B_{22}	B_{33}	B_{13}
Cu I	0.6033(1)	0.7500	0.4197(1)	0.0045	0.1298	0.0118	-0.0015
	0.6033(1)	0.7500	0.4197(1)	0.0032	0.0672	0.0082	-0.0007
	0.6031(2)	0.7500	0.4198(3)	0.0070	0.1469	0.0200	-0.0016
N(1) I	0.8120(7)	0.2500	0.6679(12)	0.0062	0.1524	0.0173	-0.0077
	0.8121(8)	0.2500	0.6695(13)	0.0053	0.1010	0.0135	-0.0051
	0.8116(10)	0.2500	0.6634(16)	0.0070	0.1838	0.0260	-0.0145
N(2) I	0.7466(5)	0.2500	0.5894(9)	0.0038	0.1154	0.0114	-0.0019
	0.7459(6)	0.2500	0.5901(9)	0.0022	0.0474	0.0100	-0.0006
	0.7465(10)	0.2500	0.5908(16)	4.624			
N(3) I	0.6780(5)	0.2500	0.5025(8)	0.0045	0.1157	0.0099	-0.0034
	0.6792(6)	0.2500	0.5027(9)	0.0030	0.0600	0.0068	-0.0024
	0.6767(9)	0.2500	0.5032(14)	4.413			
N(4) I	0.5221(4)	0.2500	0.3473(7)	0.0031	0.1262	0.0083	-0.0003
	0.5218(5)	0.2500	0.3467(8)	0.0019	0.0661	0.0049	-0.0007
	0.5241(8)	0.2500	0.3510(13)	0.0038	0.1856	0.0093	-0.0008
N(5) I	0.4696(6)	0.2500	0.2398(9)	0.0051	0.1281	0.0121	-0.0061
	0.4693(6)	0.2500	0.2381(10)	0.0035	0.0715	0.0084	-0.0025
	0.4707(11)	0.2500	0.2467(18)	0.0090	0.1232	0.0164	-0.0083
N(6) I	0.4188(14)	0.2500	0.1458(20)	0.0172	0.1773	0.0273	-0.0254
	0.4182(14)	0.2500	0.1439(18)	0.0153	0.0996	0.0186	-0.0090
	0.4203(17)	0.2500	0.1515(26)	0.0203	0.1640	0.0457	-0.0349

standard deviations given in the tables are based on refinement A.

Tables of observed and calculated structure factors are available at Chalmers University of Technology, Gibraltargatan 5A, Göteborg. Atomic coordinates and thermal parameters are given in Table 1, and bond distances and angles in Table 2. The unit cell dimensions used for the calculation of distances and angles are the average values of those obtained earlier.^{1,2} The values obtained in the two original determinations are also given in the tables for the purposes of comparison.

As expected, the values agree with those obtained previously. In the original determinations a slight difference was found in the degree of asymmetry within the two crystallographically independent azide groups. A small, though not significant,

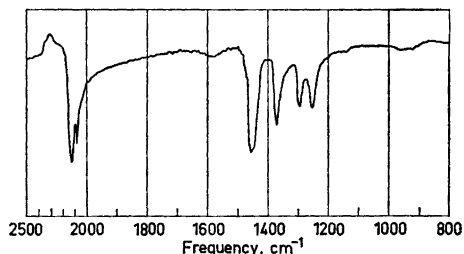


Fig. 1. Infrared spectrum of $\text{Cu}(\text{N}_3)_2$ in nujol.

difference was also found between the azide groups in the combined reflexion material. In order to obtain further information concerning bond distances within the azide ligands an IR-spectrum of

Table 2. Some important interatomic distances and angles, with their standard deviations, in $\text{Cu}(\text{N}_3)_2$. I denotes the combined determination, II² and III¹ the original, independent determinations.

Superscript	Atom at			Distance (Å)			
	none	$x,$	$y,$	$z,$	I	II	III
'		$1/2-x,$	$1/2+y,$	$1/2+z$			
"		$-x,$	$-y,$	$-z,$			
'''		$x,$	$1+y,$	z			

	Distance (Å)		
	I	II	III
Cu-N(3)	1.988(5)	1.995(5)	1.984(8)
Cu-N(4)	2.000(4)	2.003(4)	1.975(7)
Cu-N(1)'	2.555(10)	2.542(10)	2.596(15)
Cu-N(4)''	2.707(7)	2.709(7)	2.696(12)
N(1)-N(2)	1.134(12)	1.146(13)	1.097(20)
N(2)-N(3)	1.214(11)	1.199(11)	1.232(18)
N(4)-N(5)	1.206(10)	1.213(11)	1.189(20)
N(5)-N(6)	1.094(20)	1.098(16)	1.100(28)

	Angle (°)		
	I	II	III
N(1)'-Cu-N(3)	96.4(3)	96.3(3)	96.4(4)
N(1)'-Cu-N(4)	87.1(2)	87.1(3)	87.5(4)
N(3)-Cu-N(4)''	91.2(2)	91.2(3)	91.4(4)
N(4)-Cu-N(4)'''	85.2(2)	85.4(2)	84.3(4)
N(3)-Cu-N(3)'''	101.6(3)	101.0(3)	102.0(6)
N(4)-Cu-N(4)'''	100.8(3)	100.5(3)	102.6(5)
N(3)-Cu-N(4)	78.7(2)	79.2(2)	77.5(4)
Cu-N(3)-N(2)	129.1(2)	129.3(2)	128.9(3)
Cu-N(4)-N(5)	125.9(2)	126.0(3)	125.3(4)
N(1)-N(2)-N(3)	178.5(10)	177.5(11)	176.7(17)
N(4)-N(5)-N(6)	177.3(13)	176.8(14)	179.0(21)

$\text{Cu}(\text{N}_3)_2$ was registered (Fig. 1). The sample was powdered in nujol and the spectrum was registered on a Perkin-Elmer-225. The antisymmetric stretching frequency of an azide group is to be found just above 2000 cm^{-1} and the stretching frequency should increase with the asymmetry of the azide group.⁴ In the spectrum registered, the band owing to the antisymmetric stretching is split into two peaks at 2080 cm^{-1} and 2130 cm^{-1} . This may indicate that the degree of asymmetry of the groups differ, the band at 2080 cm^{-1} probably originating from the azide group with bond lengths 1.134 Å and 1.214 Å , and the band at 2130 cm^{-1} from the group with bond lengths 1.094 Å and 1.206 Å . Such a splitting of the antisymmetric stretching band has been found in $[\text{Cu}(\text{N}_3)_2(\text{NH}_3)_2]_2$,⁵ the two peaks being registered at 2040 cm^{-1} and 2080 cm^{-1} . The X-ray investigation of the latter compound also indicated that the two azide groups were different.

The least squares refinement and the calculation of bond distances and angles were performed on an IBM 360/50 computer, at the University Computing Centre, Göteborg, using the programmes LALS³ and DISTAN.²

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