erences quoted in Vols. 1–7 of *Molecular Structures and Dimensions*, 1935–1975) shows that when the co-ordination round the metal atom is trigonal bipyramidal, the nitrosyl group coordinates in a linear fashion and the IR absorption band $v(N–O)$ is found between 1770 and 1640 cm^{-1}. On the other hand, when the co-ordination round the metal atom approaches square pyramidal the nitrosyl ligand is found at the apical position and coordinates in a non-linear manner. The characteristic $v(N–O)$ band for this mode of coordination occurs in the range 1630–1654 cm^{-1} for neutral complexes and 1680–1720 cm^{-1} for cationic complexes.

In a study by English & Haines (1976) of a series of five-coordinate nitrosyls RhBr$_2$(NO)L$_2$ where L = P(Ph)$_x$(OPh)$_{3-x}$ it was found that the band $v(N–O)$ in the neutral title compound occurred at the remarkably high frequency of 1750 cm^{-1}, suggesting that this neutral complex had a trigonal bipyramidal structure. A structure determination was undertaken to ascertain whether this was in fact the case, or if the increase in $v(N–O)$ from 1630 for RhBr$_2$(NO) (PPh$_3$)$_2$ to 1750 cm^{-1} for the title compound was due to purely electronic effects.

The solution of the structure reveals a square pyramidal geometry with an apical non-linear nitrosyl group. In contrast to IrCl$_2$(NO) (PPh$_3$)$_2$ (Mingos & Ibers, 1971) the halide ligands are *cis*-disposed. The N–O vector is directed between the two Rh–P vectors, that is towards the more crowded part of the molecule. The Rh–N length is among the longest so far observed in a nitrosyl complex and is in accordance with the in-

stability of the complex with respect to decomposition products not exhibiting a $v(N–O)$ band. In IrCl$_2$(NO) (PPh$_3$)$_2$ the Ir–N length is 1·94 (2) Å.

Further work is in progress on the intermediate members of this series, which exhibit intermediate $v(N–O)$ frequencies, in order to elucidate their structures and understand more fully the role of the the P ligands in determining the molecular configuration.

References

CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* A**24**, 321–324.
CROOKS, G. R. & JOHNSON, B. F. G. (1970). *J. Chem. Soc.* (*A*), pp. 1662–1665.
ENEMARK, J. H. & FELTHAM, R. D. (1974). *Coord. Chem. Rev.* **13**, 339–406.
ENGLISH, R. B. & HAINES, R. J. (1976). To be published.
FRENZ, B. A. & IBERS, J. A. (1972). MTP *Int. Rev. Sci.* **11**, 33–72.
MINGOS, D. M. P. & IBERS, J. A. (1971). *Inorg. Chem.* **10**, 1035–1042.
Molecular Structures and Dimensions (1935–1975). Utrecht: Bohn, Scheltema and Holkema.
SHELDRICK, G. M. (1976). To be published.

Copper Complex of Guanosine-5′-monophosphate

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Abstract. [Cu$_3$(C$_{10}$H$_{12}$N$_5$O$_8$P)$_3$(H$_2$O)$_8$].5H$_2$O is ortho-rhombic, space group $P2_12_12$, with $a = 23·369$ (5), $b = 20·711$ (5), $c = 11·305$ (3) Å, $Z = 4$, $D_m = 1·81$ (3), $D_x = 1·83$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0·71069$ Å. There are three Cu(5′-GMP) complexes in the asymmetric unit linked together *via* base–Cu–phosphate bonds forming a polymeric chain. Cu has square pyramidal five-coordination with the binding axially through N(7).

Introduction. Single crystals of octahedral habit were obtained by mixing equimolar quantities of disodium guanosine-5′-phosphate and Cu(NO$_3$)$_2$ in water. The amount of crystalline material was not enough to carry out an elementary analysis. A crystal was mounted along **c** and data within a sphere of reflexions limited at sin $\theta/\lambda = 0·56$ were collected on a Siemens diffractometer. The experimental procedure is described elsewhere (Sletten, 1974). Of the 6460 unique reflexions recorded, 1999 were less than the threshold value.

The structure was solved by *MULTAN* (Main, Woolfson, Lessinger, Germain & Declercq, 1974) and refined by full-matrix least squares to an R of 0·077. Due to limited computer space each cycle had to be run in three passes. Cu and P were refined anisotropically, the other atoms isotropically. 52 of the 62 H atoms were located in a difference map and included in the structure factor calculations, but not refined. The 10 remaining H atoms belong to the crystal water.

Table 1. *The final atomic parameters*

(a) Atoms refined anisotropically

Temperature parameters $\times 10^4$, positional parameters $\times 10^5$. Standard deviations are in parentheses. Anisotropic temperature factor $= \exp\left[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{23}klb^*c^* + 2U_{13}hla^*c^*)\right]$.

	X/a	Y/b	Z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{23}	U_{13}
Cu(1)	17468 (7)	5696 (7)	25726 (13)	268 (8)	194 (8)	232 (8)	15 (8)	1 (7)	−36 (7)
Cu(2)	17341 (7)	41241 (7)	34851 (13)	215 (7)	186 (9)	225 (7)	4 (7)	5 (7)	−24 (7)
Cu(3)	37167 (7)	20021 (7)	68407 (14)	245 (8)	199 (8)	256 (8)	−10 (7)	−9 (7)	−20 (7)
P(1)	31282 (13)	6198 (16)	61542 (28)	187 (18)	155 (16)	230 (17)	−2 (14)	4 (14)	−16 (13)
P(2)	30212 (13)	40617 (16)	71288 (28)	174 (23)	144 (22)	254 (20)	−25 (11)	24 (12)	−22 (15)
P(3)	23085 (14)	26934 (16)	31340 (30)	229 (24)	160 (20)	228 (23)	16 (15)	28 (10)	13 (20)

(b) Atoms refined isotropically

Temperature parameters $\times 10^3$, positional parameters for N, C, O $\times 10^4$, for H $\times 10^3$. Isotropic temperature factor $= \exp\left[-8\pi^2 U \sin^2 \theta / \lambda^2\right]$. Standard deviations in coordinates and temperature parameters for non-hydrogen atoms, except crystal water, are in the range 0·007–0·016 Å and 0·002–0·003 Å², respectively. For the crystal water the corresponding values are approximately doubled.

	Molecule 1				Molecule 2				Molecule 3			
	X/a	Y/b	Z/c	U	X/a	Y/b	Z/c	U	X/a	Y/b	Z/c	U
N(1)	−410	891	3822	25	−408	4208	5085	27	5851	2397	5656	21
N(2)	−1061	995	5356	25	−1034	4176	6716	51	6515	2656	4171	31
N(3)	−108	894	5815	24	−66	4070	7059	27	5550	2685	3692	24
N(7)	1146	691	4058	27	1163	4094	5136	24	4283	2329	5366	22
N(9)	918	787	5978	22	960	3948	7074	26	4527	2628	3520	23
C(2)	−508	938	5007	27	−489	4152	6292	26	5983	2596	4499	20
C(4)	404	826	5347	24	448	4053	6518	19	5046	2566	4151	22
C(5)	576	763	4159	23	569	4145	5353	25	4889	2406	5275	23
C(6)	143	790	3311	20	122	4215	4524	27	5319	2317	6120	27
C(8)	1342	726	5141	26	1378	3964	6199	22	4080	2484	4311	27
C(1')	969	886	7263	26	1068	3774	8318	34	4464	2874	2308	30
C(2')	1025	240	7934	28	1372	3140	8492	24	4312	2364	1341	43
C(3')	1664	192	8122	27	1725	3244	9610	27	3682	2490	1271	34
C(4')	1854	916	8239	20	1850	3964	9524	27	3609	3190	1427	24
C(5')	2447	1031	7863	33	2433	4135	9090	31	3042	3401	1949	36
O(6)	172	731	2222	34	132	4268	3448	35	5292	2160	7178	34
O(1')	1457	1241	7486	29	1422	4260	8814	30	4049	3349	2310	29
O(2')	730	312	9023	50	985	2624	8588	45	4591	2535	275	80
O(3')	1819	−160	9180	41	1399	3089	10639	37	3434	2297	168	58
O(5')	2533	881	6654	28	2533	3810	7959	25	2914	3049	3014	26
O(4)	2992	431	4911	28	2951	3648	6049	24	2394	2183	4078	21
O(7)	3565	1151	6217	27	2895	4771	6894	29	1872	3207	3499	28
O(8)	3321	51	6900	30	3607	3967	7718	27	2154	2412	1950	32
O(1)	2427	1000	3191	31	2447	4299	4357	29	3784	2727	7937	46
O(2)	1560	1343	1727	64	1120	4012	2322	29	4292	1641	7915	37
O(3)	1187	130	1536	31					3010	2369	6131	28
H(1)	−78	100	307	40	−72	420	537	45	625	226	613	45
H(21)	−108	104	605	40	−136	433	616	38	681	270	488	40
H(22)	−141	112	489	40	−125	415	740	72	655	283	370	84
H(8)	177	70	550	40	181	383	638	27	359	255	379	45
H(1')	66	113	759	40	67	372	872	19	485	308	210	43
H(2')	45	80	858	45	95	240	770	85	464	300	30	45
H(O2')	89	−10	730	40	164	295	785	72	454	204	187	45
H(3')	150	−36	970	45	167	288	115	24	355	184	10	45
H(O3')	190	1	733	40	207	292	950	26	336	236	173	20
H(4')	192	102	904	40	175	418	1033	53	375	340	50	45
H(5'1)	272	80	830	40	270	402	967	45	277	343	134	45
H(5'2)	255	151	801	40	240	465	907	45	311	386	217	45
H(11)	240	143	330	56	268	−36	541	45	380	321	770	56
H(12)	265	70	380	45	245	405	495	69	346	261	831	45
H(21)	175	180	178	45	70	401	257	32	468	190	765	45
H(22)	135	145	110	60	100	360	220	45	441	130	762	52
H(31)	80	33	170	45					303	275	607	45
H(32)	387	461	825	71					260	205	580	45
O(W1)	4667	4155	61	82								
O(W2)	679	1811	499	109								
O(W3)	2833	1276	598	170								
O(W4)	3742	584	760	170								
O(W5)	4188	372	8506	103								

Atomic parameters are listed in Table 1.* Scattering factors and computer programs are mentioned elsewhere (Sletten, 1974).

Discussion. The bond lengths in the coordination spheres and phosphate groups are shown in Fig. 1. The molecular dimensions of the guanosines have standard deviations too large to warrant listing ($\sigma_l \simeq 0.02$ Å). Each guanine base is attached at the N(7) position to a Cu atom, which in turn is bonded to a phosphate group of a neighbouring GMP. The Cu ions have slightly irregular square pyramidal $(4+1)$ coordination with the base N in the axial position and the equatorial positions occupied by phosphate and water O atoms. The four equatorial ligands are approximately coplanar, with Cu displaced out-of-plane towards the axial ligand.

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31912 (42 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.
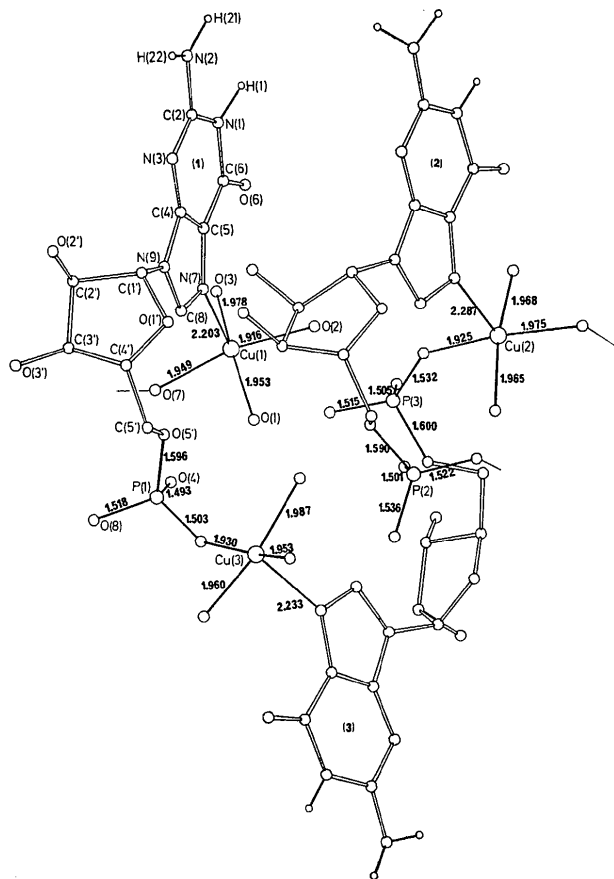
Fig. 1. One asymmetric unit of Cu(5'-GMP) showing bond distances in the coordination sphere and in the phosphate groups. In the polymeric chain phosphate group P(2) is coordinated to Cu(1) via O(7) and phosphate group P(1) is coordinated to Cu(3) as shown and to Cu(2) via O(8). The estimated standard deviations are in the range 0·008–0·010 Å.
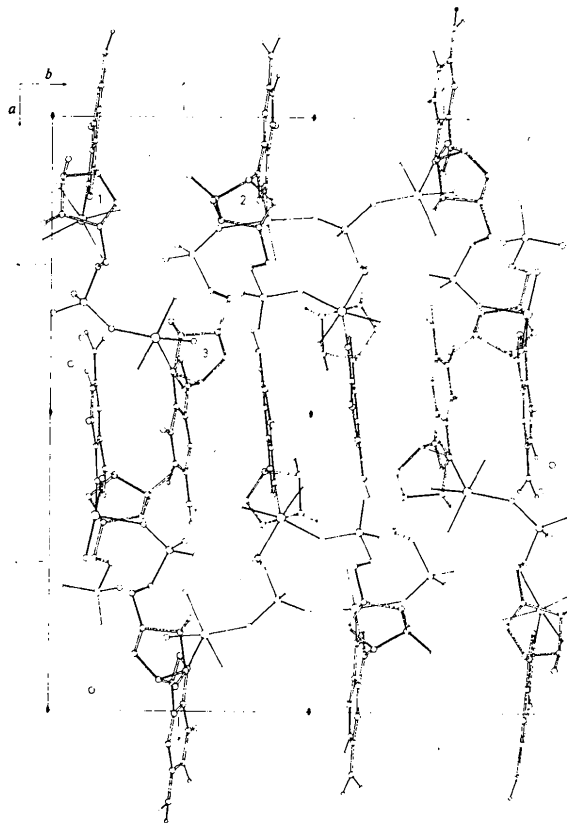
Fig. 2. The *ab* projection of the unit cell showing the two parallel helical chains running along the *b* axis.

The nucleotides are all in the *anti* configuration. The puckerings of the ribose rings are C(3')-*endo* for rings 1 and 3 and C(2')-*endo*–C(3')-*exo* for ring 2. The conformation about the phosphate–ribose bond, C(4')–C(5'), is *gauche–gauche* for all three molecules.

The packing in the crystal is shown in Fig. 2. The nucleotides are linked by alternating base–metal–phosphate bonds forming an infinite helical chain about a crystallographic twofold screw axis. The individual nucleotides in the trimer are positioned so as to make the screw pitch of the helix $\frac{1}{3}$ of *b*. The base planes of two adjacent helical chains are interleaved so as to form a stacking pattern comparable to that in DNA. The bases are almost parallel with an average interplanar distance of 3·4 Å. The two strands are held together *via* strong dihydrogen bonds between guanine and phosphate. As pointed out previously, only guanine has the ability to form such dihydrogen bonds to oxyanions (Sletten & Fløgstad, 1976). In Fig. 3 a stereo picture of the cell viewed along the screw axis gives an impression of how the nucleotide chain is wound in a right-handed helical arrangement. The distance across the double stack is approximately 20 Å which is almost identical to the corresponding dimension for double helical DNA.

The structural results of the present investigation have been discussed in relation to structures of Cu complexes of nucleoside analogues (Sletten, 1976).
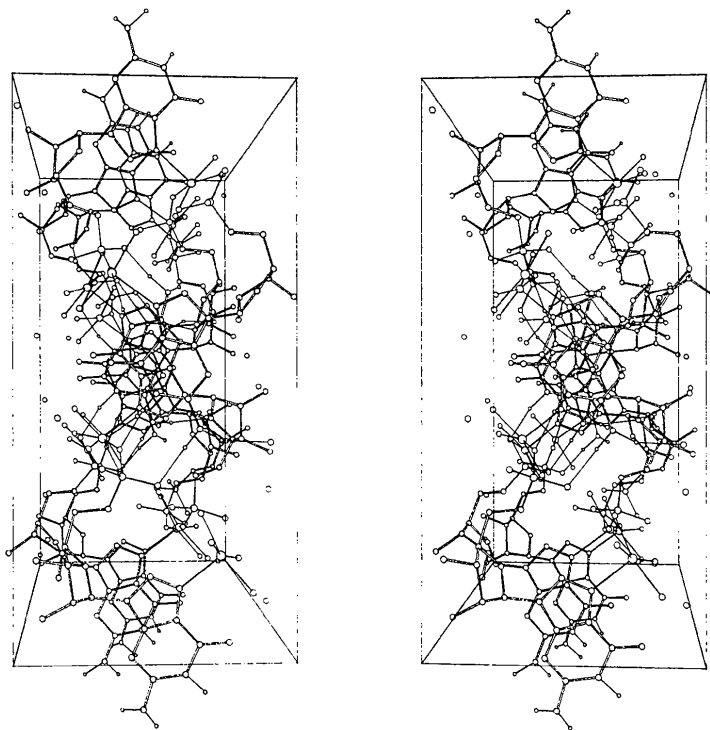
Fig. 3. Stereoscopic drawing of the unit cell viewed down the c axis.

References

MAIN, P., WOOLFSON, M. M., LESSINGER, L., GERMAIN, G. & DECLERCQ, J. P. (1974). *MULTAN, A System of Computer Programs for the Automatic Solution of Non-centrosymmetric Crystal Structures*. Univs. of York and Louvain.

SLETTEN, E. (1974). *Acta Cryst.* B30, 1961–1966.
SLETTEN, E. (1976). In *Metal–Ligand Interaction in Organic Chemistry and Biochemistry*, 9th Jerusalem Symp. Quant. Chem. Biochem., Israel Academy of Sciences and Humanities. In the press.
SLETTEN, E. & FLØGSTAD, N. (1976). *Acta Cryst.* B32, 461–466.

Diacetyltylophorinidine Methiodide*

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Abstract. $C_{27}H_{30}NO_6I$, $M = 591\cdot4$, monoclinic, $C2$, $a = 26\cdot89$ (1), $b = 12\cdot35$ (1), $c = 16\cdot62$ (1) Å, $\beta = 109$ (1)°, $Z = 8$, $D_m = 1\cdot52$ (1), $D_x = 1\cdot51$ (1) g cm^{-3}, $F(000) = 2400$, $\mu(Cu\ K\alpha) = 102\cdot3$ cm^{-1}. Tylophorinidine, a potential anti-cancer phenolic alkaloid isolated from the plant *Tylophora asthmatica*, is shown to be 6,6'-di-hydroxy-3,7-dimethoxyphenanthro[9,10:6',7']indolizidine. Its absolute configuration was also determined.

Introduction. Tylophorinidine was first isolated by Mulchandani, Iyer & Badheka (1971) from *Tylophora asthmatica*, a plant used indigenously in the treatment of allergic rhinitis and bronchial asthma. Structure (I) was assigned to it by these authors. However, this could not be considered unambiguous (Wadhawan,

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* A preliminary report of this study has already been published (Wadhawan, Sikka & Mulchandani, 1973).