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Tungsten Carbonyl Complexes of 2′,3′-O-Isopropylideneguanosine and 6-Mercaptopurine

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Purine substituted tungsten carbonyls are shown to be useful model compounds for studying metal binding sites of nucleic acid components. Elemental analysis, molecular weight determinations, ^1H *nmr and ir data reveal that 6-mercaptopurine is capable of acting both as a monodentate S(6)-bonded and bidentate S(6)–N(7)-bonded ligand to give the complexes* $W(CO)_5L$ *and* $W(CO)_4L$*, respectively. 2′,3′-O-isopropylideneguanosine behaves as a monodentate ligand to yield the pentacarbonyl complex* $W(CO)_5L$*.*

Introduction

We were interested in the synthesis and spectroscopic characterization of coordination compounds of the nucleic acid components [1, 2]. These moieties afford a large number of coordination possibilities including chelation and bridging between metal ions. Guanosine has been shown to be particularly interesting, because different experiments have pointed to the guanine base as the preferred site of attack by antineoplastic platinum compounds on DNA [3–5]. Since only the bifunctional *cis*-$PtCl_2(NH_3)_2$ shows anti-tumor activity [6, 7] while the monofunctional *trans* isomer has virtually none, it has been inferred that the different physiological effects of these two isomers are associated with the ability of guanosine to form a N(7)–O(6) chelate with the active Pt-drug [8, 9].

However, the exact nature of metal binding in such complexes is not yet firmly established and the conclusions are not in agreement as to whether this nucleoside acts as monodentate or bidentate ligand. On the basis of spectroscopic results chelation has been suggested in some cases [8–15] but in X-ray structural determinations a five membered chelate ring has not been found [16, 17]. A critical summary on this subject has been given by Tobias [18].

Since much attention has been focussed on the mode of binding in purine derivatives we have attempted to design simple experiments to obtain information about the coordination site of nucleic acid components. The principal method applied is that substitution reactions between group VI metal carbonyls and heterocycles occur fairly readily and the final substitution products can be easily distinguished by infrared spectroscopy. Chelating ligands react with metal hexacarbonyls to give tetracarbonyl derivatives $M(CO)_4L$ while monodentate ligands produce the pentacarbonyl species $M(CO)_5L$.

Experimental

Tungsten hexacarbonyl, isopropylideneguanosine, 6-mercaptopurine and DMSO-d_6 were purchased commercially and used without further purification. Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer; spectra of solids were obtained as KBr pellets while solution spectra were solvent compensated. ^1H nmr spectra were obtained with a Varian A 60 instrument (60 Mc/s). Molecular weights were measured on a Mechrolab Osmometer in acetone solution. Decomposition points were determined using a Büchi melting point apparatus and were uncorrected.

Preparation of Complexes

All experiments were carried out under an atmosphere of pure dry nitrogen. Solvents were dried by standard procedures and distilled under nitrogen before use.

The complexes are stable in the solid state for several months but they decompose slowly in solution. They are soluble in ether, tetrahydrofuran, methanol, acetone and dimethyl sulfoxide and insoluble in water, benzene and petroleum ether. The carbonyls exhibit no characteristic melting points and decompose above 150 °C.

Pentacarbonyl(2′,3′-O-isopropylideneguanosine)-tungsten(0)

$W(CO)_6$ (2.10 g, 6 mmol) and 2′,3′-isopropylideneguanosine (0.69 g, 3 mmol) were heated together in ethyleneglycol monomethylether (10 ml) at 130 °C for 45 min during which time the theoretical amount of CO was evolved. Solvent and excess of $W(CO)_6$

TABLE I. Analytical Data.

Compound	Formula	Mol Wt[a]		C%		H%		N%	
		calcd.	found	calcd.	found	calcd.	found	calcd.	found
$W(CO)_5$(Isopropylideneguanosine)	$WC_{18}H_{17}N_5O_{10}$	647.2	670	33.40	34.29	2.65	3.55	10.82	10.80
$W(CO)_5$(6-Mercaptopurine)•ethyleneglycol monomethylether	$WC_{10}H_4N_5O_5S$	494.1	501	27.38	26.89	2.12	1.28	9.83	9.78
$W(CO)_4$(6-Mercaptopurine)•0.5 ether	$WC_9H_4N_5O_4S$	466.1	448	26.23	26.15	1.80	2.01	11.13	11.23

[a]Without solvent of crystallization; osmometric in acetone.

were removed under vacuum at 100 °C. The residual yellow-brown solid was dissolved in acetone (15 ml) and the opaque solution purified with active carbon to give a clear yellow solution. On addition of n-pentane (*ca.* 10–20 ml) an oily precipitation was formed which was removed by centrifugation. To the centrifuged solution, small volumes of n-pentane were carefully added (*ca.* 50 ml in all). After a few minutes yellow needle-like crystals separated which were collected and dried *in vacuo* for several hours (yield 1.0 g, 51%).

Pentacarbonyl(6-mercaptopurine)tungsten(0)

$W(CO)_6$ (1.05 g, 3 mmol) was dissolved in tetrahydrofuran (200 ml) and the solution irradiated for 1 h with an ultraviolet lamp following the general method of Strohmeier [19]. The ligand 6-mercaptopurine (0.85 g, 5 mmol) dissolved in ethyleneglycol monomethylether (30 ml) was added to the yellow solution and the mixture stirred for 5 minutes. The solvent was removed under high vacuum at room temperature. The resultant red oil was dissolved in ether and filtered through cellulose to give a yellow solution which was reduced in volume to 20 ml. On addition of n-pentane a yellow oil [20] was formed; it solidified on drying *in vacuo* at room temperature (yield 2.0 g, 80%).

Tetracarbonyl(6-mercaptopurine)tungsten(0)

$W(CO)_6$ (1.76 g, 5 mmol) and 6-mercaptopurine (0.85 g, 5 mmol) were heated together in ethyleneglycol monomethylether (40 ml) at 130 °C. The solution turned red within 10 min, indicating the formation of (6-mercaptopurine)$W(CO)_4$. The reaction was complete after 1–1 ½ h. The solvent was completely removed under vacuum at 100 °C. The residual red-brown solid was dissolved in ether and filtered through cellulose. The orange-red filtrate was concentrated and the brick-red product was precipitated by adding n-pentane. The product was collected and dried *in vacuo* for several hours (yield 1.3 g, 55%).

Results and Discussion

Complex with 2′,3′-O-isopropylideneguanosine

Heating of tungsten hexacarbonyl with 2′,3′-O-isopropylideneguanosine in ethyleneglycol monomethylether leads to the separation of lemon-yellow needle-like crystals of pentacarbonyl(2′,3′-O-isopropylideneguanosine)tunsten(0):

$$W(CO)_6 + L \xrightarrow{\Delta T} W(CO)_5L + CO$$

(L = 2′,3′-O-isopropylideneguanosine)

$W(CO)_5L$ is characterized by three ν(W)CO absorptions having weak, very strong and strong intensities

TABLE II. Carbonyl Stretching Frequencies (in THF) and Far Infrared Spectra (in KBr) of Substituted Tungsten Hexacarbonyls.

Compound	ν(M)CO[a]				δMCO[a]			νM–CO[a]
	A_1	B_1	E	A_1				
$W(CO)_5$(Isopropylideneguanosine)	2070	1973	1925	1880	600	590	550	363
$W(CO)_5$(6-Mercaptopurine)	2070	1972	1925	1887		588	546	368
	A_1	A_1	B_1	B_2				
$W(CO)_4$6-Mercaptopurine	2006	1882	1882	1834				358

[a]Intensities, see Fig. 1 and 3.

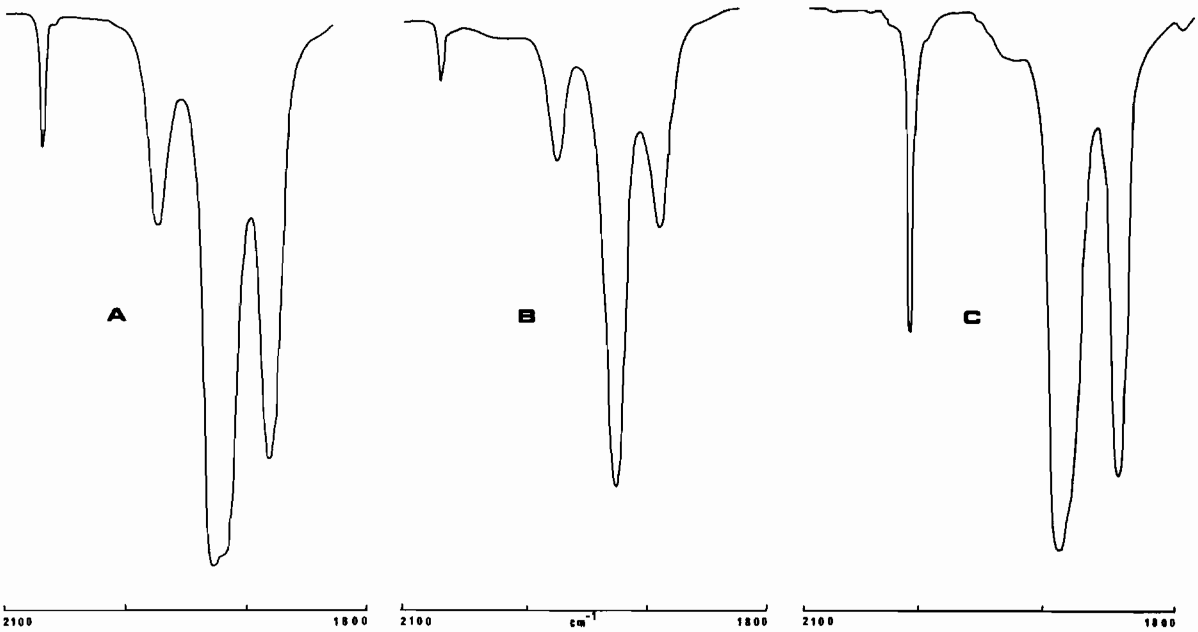


Fig. 1. Infrared spectra of $W(CO)_5$(isopropylideneguanosine) (A), $W(CO)_5$(6-mercaptopurine) (B) and $W(CO)_4$(6-mercaptopurine) (C) in the 2100–1800 cm^{-1} range (in THF).

(Fig. 1, Table II). These absorptions are assigned to the A_1, E and A_1 vibrational modes, respectively. In addition to these three absorptions the spectrum contains a band at 1973 cm^{-1}. The position of this band is assigned to the forbidden B_1 mode which is frequently found in this region. The δ(WCO) and νW–CO vibrations are in the same frequency region as observed for other monosubstituted hexacarbonyls [21–23].

The mode of bonding between the 2′,3′-O-isopropylideneguanosine and metal is easily derived. $W(CO)_5$ is monofunctional and it is apparent that the coordinated nucleoside has to be bonded as a monodentate ligand. The possible monodentate coordination sites are the exocyclic nitrogen and oxygen atom attached to the heterocyclic ring system. In order to determine the actual donor group the ir spectra of the free and coordinated ligand are compared. The areas of interest are the νNH_2 present at 3100–3500 cm^{-1} and the νCO present at 1700 cm^{-1}.

Several investigations have shown that the νNH_2 stretching frequencies of amines are shifted to lower frequency on coordination by as much as 200 cm^{-1} [24–26]. Isopropylideneguanosine has two broad bands in the νNH_2 region at 3300 and 3165 cm^{-1}. In the carbonyl complex the νNH_2 stretching modes are shifted to higher frequency by about 100 cm^{-1} (Fig. 2). A positive shift of this magnitude strongly suggests that this purine nucleoside is not NH_2-bonded.

The spectral features in the 1500–1700 cm^{-1} range are illustrated in Fig. 2. There are no significant differences between the spectra of the free and the coordinated ligand indicating a non-involvement of the exocyclic oxygen atom. A metal–O(6) interaction would shift the frequency of the nucleoside vibration at *ca.* 1700 cm^{-1} to significantly lower wavenumbers.

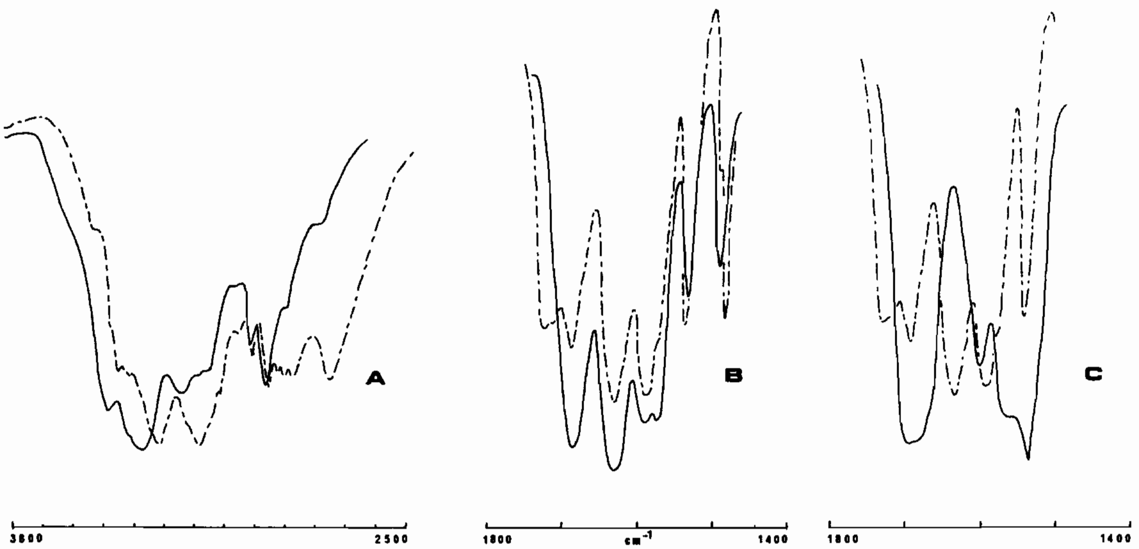


Fig. 2. Infrared spectra in the 3800–2500 (A) and 1800–1400 cm^{-1} (B) region of isopropylideneguanosine before (– – – –) and after (————) interacting with $W(CO)_5$; deuterated isopropylideneguanosine (C) (in KBr).

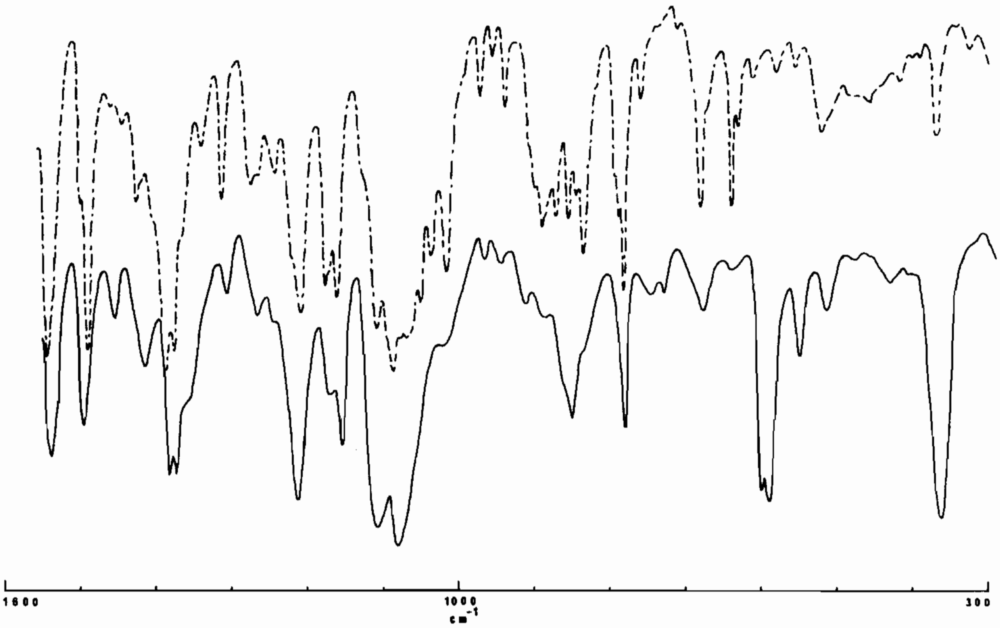


Fig. 3. Infrared spectra of free (– – – –) and coordinated (————) isopropylideneguanosine in the 1600 to 300 cm^{-1} range (in KBr).

This mode is almost a pure νCO stretching and appears at 1665 cm^{-1} in D_2O solution [27]. In the solid state the spectrum is complicated by a splitting of this band into a doublet at 1730 and 1690 cm^{-1} probably due to lattice effects. In the deuterated compound the doublet is replaced by a broad asymmetric band at 1700 cm^{-1} (in KBr). In $W(CO)_5$(isopropylideneguanosine) this band is *ca.* 10 cm^{-1} lower and increases by 2 and 30 cm^{-1} in chloroform and THF solution, respectively. The higher νC=O stretching frequency observed for THF solution may be due to a lesser hydrogen bonding with the solvent molecules. The high position of the carbonyl band indicates that bound isopropylideneguanosine has a keto structure and is protonated at N(1). The 1700 cm^{-1} band would disappear when the proton is transferred from N(1) [28]. The removal of the band at 1630 cm^{-1} on deuteration supports the assignment of δNH_2 deformation vibration to this absorption. A similar assignment of δNH_2 was given by Miles *et al.* [27] on the basis of deuteration studies in dimethylsulfoxide.

TABLE III. Proton Chemical Shifts Relative to TMS (δ, in ppm) for DMSO-d_6 Solutions of Free and Coordinated Isopropylideneguanosine and 6-Mercaptopurine.

Compound	H(2)	H(8)	=NH	$-NH_2$	H(1)	H(2)	H(3)	H(4)	H(5)	$=C(CH_3)_2$	
Isopropylideneguanosine		7.98	10.82	6.55	5.97[a]	5.23	5.08	4.20	3.57	1.50	1.30
$W(CO)_5$(Isopropylideneguanosine)		8.73	10.97	6.80	6.07	5.27	5.07	4.23	3.63	1.53	1.33
6-Mercaptopurine	8.55	8.40	8.33								
$W(CO)_5$(6-Mercaptopurine)	9.23	8.60	14.37								
$W(CO)_4$(6-Mercaptopurine)	8.70	9.03	11.30								
6-Methylmercaptopurine	8.78	8.46									

[a]Doublet $J_{1'2'} = 3$ Hz.

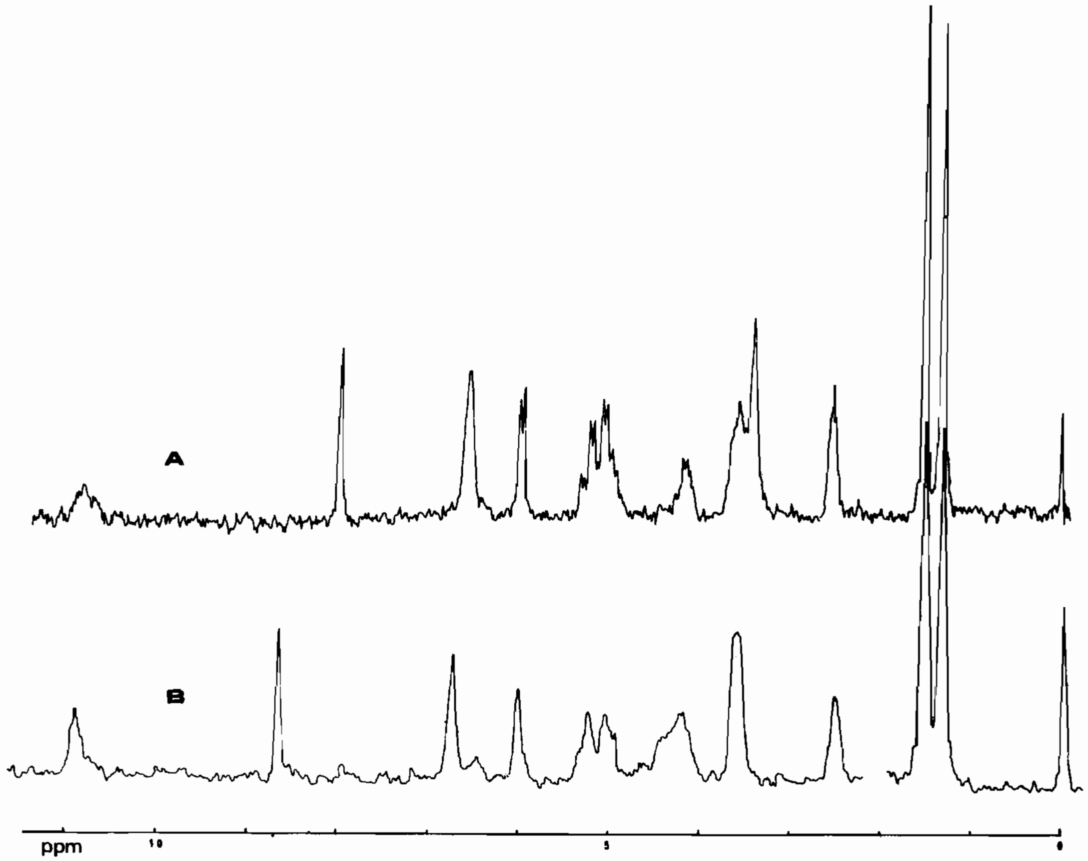
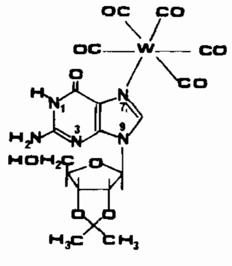


Fig. 4. ^1H nmr spectra of free (A) and coordinated (B) isopropylideneguanosine in DMSO-d_6 solution (δ, ppm).

The ir spectra show that both exocyclic N- and O-donor atoms are not involved in coordination and the metal coordination is limited to the endocyclic nitrogen atoms N(3) and N(7). Unfortunately coordination of $W(CO)_5$ to the heterocyclic ring causes minor perturbation of the ligand vibration in the fingerprint (Fig. 3) and information whether the metal binds to the five- or six-membered ring of the base portion is difficult to obtain. However, on the basis of simple steric arguments coordination of isopropylideneguanosine through N(3) appears unlikely leaving N(7) as the favored binding position.

Nmr studies on guanosine in DMSO confirm that N(7) is involved in coordination. Protons attached to carbon atoms that are closest to the binding site are known to shift more downfield than others [29, 30].

The spectra of free and bound isopropylideneguanosine are shown in Fig. 4. The signals due to ribose protons are broadened but not shifted noticeably on coordination. The nitrogen-bound protons do not move downfield significantly while the H(8) resonance is shifted downfield the most. Similar trends have been observed for several guanosine complexes where the shift displacement of H(8) by *ca.* 0.5–0.7 ppm has been ascribed to metal binding via N(7) [2, 18, 31–34]. The proposed structure of $W(CO)_5$(isopropylideneguanosine) is shown below.



Attempts to prepare the chelate complex $W(CO)_4$-(guanosine) by thermal or photochemical reactions were unsuccessful.

Complexes with 6-mercaptopurine

Unlike 2′,3′-O-isopropylideneguanosine, 6-mercaptopurine leads to the formation of two types of compounds when treated with tungsten hexacarbonyl. The first type of complex is prepared by adding the heterocyclic ligand to an irradiated solution of $W(CO)_6$ in THF (Eq. 1). The yellow product formed is monomeric (Table I) and the positions and intensities of the carbonyl absorptions are characteristic of a pentacarbonyl complex $W(CO)_5L$ in an octahedral environment (Fig. 1). The assignment of the $2A_1$ and E bands is analogous to that of $W(CO)_5$(isopropylideneguanosine). The second type of derivative is synthesized by direct thermal reaction in ethyleneglycol monomethylether (Eq. 2). The analytical data (Table I) show that this monomeric brick-red complex contains four CO-groups and one 6-mercaptopurine ligand bonded to the central atom. The ir spectrum (Fig. 1) is characteristic of the *cis*-arrangement of the four CO-ligands. The assignment of the νMCO modes $2A_1$, B_1 and B_2 for C_{2v} symmetry is according to other disubstituted hexacarbonyls [21, 35, 36]. However one of the A_1 bands and the B_1 band are not resolved; the overlapping of these two absorptions has also been observed in several tetracarbonyl compounds [35, 36]. The above reactions indicate that 6-mercaptopurine behaves as both monodentate and bidentate ligand. Direct irradiation of $W(CO)_6$ in the presence of 6-mercaptopurine affords a mixture containing penta- and tetracarbonyl complexes (Eq. 3), implying that chelate formation of the purine ligand in $W(CO)_4L$ proceeds most likely through a monodentate interaction first, followed by ring closure with displacement of a second CO group.

$$W(CO)_6 \xrightarrow[-CO]{THF/h\nu} W(CO)_5THF \xrightarrow{L} W(CO)_5L \quad (1)$$

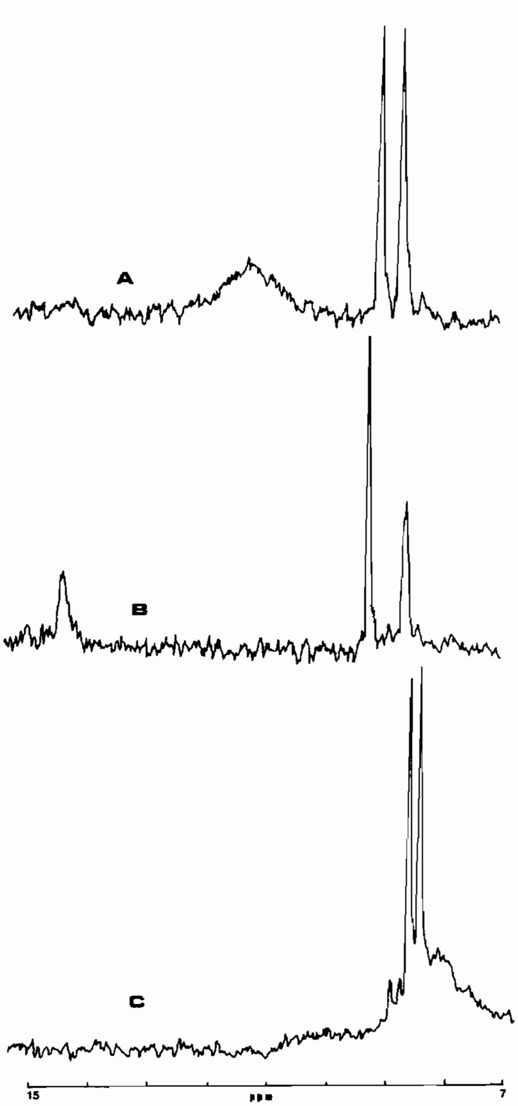


Fig. 5. Nmr spectra in the aromatic proton region of $W(CO)_4$-(6-mercaptopurine) (A), $W(CO)_5$(6-mercaptopurine) (B) and 6-mercaptopurine (C) in DMSO-d_6 solution (δ, ppm).

$$W(CO)_6 + L \xrightarrow[-2CO]{\Delta T} W(CO)_4L \quad (2)$$

$$W(CO)_6 + L \xrightarrow{h\nu} W(CO)_5L + W(CO)_4L \quad (3)$$

L = 6-mercaptopurine

The effect of coordination on the chemical shifts of 6-mercaptopurine is shown in Fig. 5. The 0.48 ppm downfield shift of H(2) relative to H(8) on formation of $W(CO)_5$ (6-mercaptopurine) is virtually the same as for the electrophilic attack of CH_3^+ on the purine base at the S(6) position [37]. It is reasonable to assume that $W(CO)_5$(6-mercaptopurine) has the heterocyclic ligand coordinated via S(6). This mode of binding is also consistent with the well known affinity of "soft" metals for sulfur

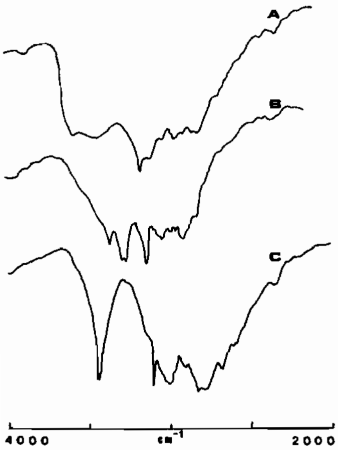


Fig. 6. Infrared spectra of $W(CO)_4$(6-mercaptopurine) (A), $W(CO)_5$(6-mercaptopurine) (B) and 6-mercaptopurine (C) in the 4000–2000 cm^{-1} range (in KBr).

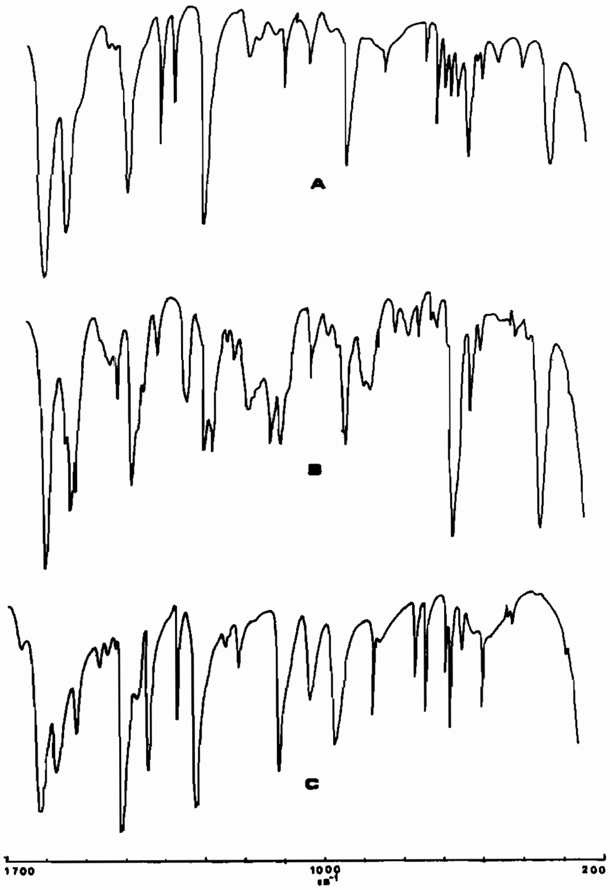
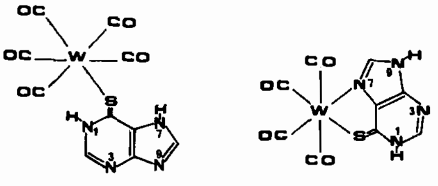


Fig. 7. Infrared spectra of $W(CO)_4$(6-mercaptopurine) (A), $W(CO)_5$(6-mercaptopurine) (B) and 6-mercaptopurine (C) in the 1700 to 200 cm^{-1} range (in KBr).

donors. An analogous monodentate binding involving the exocyclic C(6)S group has previously been reported for $HgCl_2$(6-mercaptopurine) [38].

The ^{1}H nmr spectrum of $W(CO)_4$(6-mercaptopurine) is shown in Fig. 5. As a bidentate ligand, 6-mercaptopurine has three possible binding sites, N(1)–S(6), N(3)–N(9), and N(7)–S(6). Of these, the N(3)–N(9) and N(1)–S(6) sites seem very unlikely because a five-membered chelate ring N(7)–S(6) will have less internal strain than the four-membered ring. This basis provides information for assigning the two aromatic protons H(2) and H(8). The downfield shifts caused by metal binding are 0.63 ppm and 0.15 ppm (Table III). As outlined above, the largest shift change occurs for the H(8)proton next to the coordination site, giving a shielding order H(2) > H(8). This order is reversed to that of the free ligand [39] and has been found when protonation or alkylation are directed to the imidazole ring [40].

No absorption attributable to SH stretching is observed at *ca.* 2500 cm^{-1} in the ir spectra of free and coordinated 6-mercaptopurine (Fig. 6) and it can be assumed that the C(6)–S bond retains appreciable double bond character in the structures A and B; the thione form of the free crystalline ligand is established by X-ray structure determinations [41, 42].



A B

It is generally observed that skeletal stretching motions in purine bases increase in energy upon complexation or protonation [30, 43–45]. The highest frequency ring mode in 6-mercaptopurine appears at 1613 cm^{-1} (in KBr) (Fig. 7) and shifts to 1583 cm^{-1} on deprotonation [2]. In $Rh(CO)(PPh_3)_2$(6-mercaptopurinate) this band is found at 1600 cm^{-1} [2] and increases in frequency to 1610 and 1620 cm^{-1} in $W(CO)_5$(6-mercaptopurine) and $W(CO)_4$(6-mercaptopurine), respectively. A similar trend is found for the band at *ca.* 1400 cm^{-1}.

Acknowledgements

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References

1 Part 15: Metal Complexes with Biologically Important Ligands; Part 14: W. Beck, J. C. Calabrese and N. Kottmair, *Inorg. Chem., 18,* 176 (1979).
2 W. Beck and N. Kottmair, *Chem. Ber., 109,* 970 (1976).

3 R. Bau, R. W. Gellert, S. M. Lehovec and S. Louie, *J. Clin. Hematol. Oncol.*, *7*, 51 (1977) and refs. therein.
4 K. P. Beaumont, C. A. McAuliffe and M. E. Friedman, *Inorg. Chim. Acta*, *25*, 241 (1977) and refs. therein.
5 S. Mansy, G. Y. H. Chu, R. E. Duncan and R. S. Tobias, *J. Am. Chem. Soc.*, *100*, 607 (1978) and refs. therein.
6 T. A. Connors and J. J. Roberts, Ed., 'Platinum Coordination Complexes in Cancer Chemotherapy', Springer Verlag Heidelberg (1974).
7 A. Khan, Ed., 'Proceedings of the Third International Symposium on Platinum Coordination Complexes in Cancer Chemotherapy', *J. Clin. Hematol. Oncol.*, 7 (1977).
8 J. P. Macquet and T. Theophanides, *Bioinorg. Chem.*, *5*, 59 (1976).
9 M. M. Millard, J. P. Macquet and T. Theophanides, *Biochim. Biophys. Acta*, *402*, 166 (1975).
10 L. G. Marzilli, *Prog. Inorg. Chem.*, *23*, 255 (1977) and refs. therein.
11 A. T. Tu and M. J. Heller, in 'Metal Ions in Biological Systems', H. Sigel, Ed., Marcel Dekker, New York (1974) 1, p. 35 and refs. therein.
12 D. M. L. Goodgame, J. Jeeves, F. L. Phillips and A. C. Skapski, *Biochim. Biophys. Acta*, *378*, 153 (1975).
13 J. Dehand and J. Jordanov, *Chem. Commun.*, 598 (1976).
14 R. Cini, P. Colamarino and P. L. Orioli, *Bioinorg. Chem.*, *7*, 345 (1977).
15 G. Pneumatikakis, N. Hadjiliadis, and T. Theophanides, *Inorg. Chem.*, *17*, 915 (1978).
16 D. J. Hodgson, *Prog. Inorg. Chem.*, *23*, 211 (1977) and refs. therein.
17 R. E. Cramer and P. L. Dahlstrom, *J. Clin. Hematol. Oncol.*, *7*, 330 (1977).
18 G. Y. H. Chu, S. Mansy, R. E. Duncan and R. S. Tobias, *J. Am. Chem. Soc.*, *100*, 593 (1978).
19 W. Strohmeier and F. J. Müller, *Chem. Ber.*, *102*, 3608 (1969).
20 The product contained some ethyleneglycol monomethylether which could not be removed by heating *in vacuo* as the pentacarbonyl evolved CO at higher temperature to give the tetracarbonyl complex.
21 D. M. Adams, 'Metal–Ligand and Related Vibrations', E. Arnold, London (1967).
22 R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, *6*, 65 (1972).
23 M. A. M. Meester, R. C. J. Vriends, D. J. Stufkens and K. Vrieze, *Inorg. Chim. Acta*, *19*, 95 (1976).
24 L. F. Lindoy, S. E. Livingstone and T. N. Lockyer, *Aust. J. Chem.*, *20*, 471 (1967).
25 G. F. Svatos, C. Curran and J. V. Quagliano, *J. Am. Chem. Soc.*, *77*, 6159 (1955).
26 M. A. J. Jungbauer and C. Curran, *Spectrochim. Acta*, *21*, 641 (1965).
27 H. T. Miles, F. B. Howard and J. Frazier, *Science*, *142*, 1458 (1963).
28 T. Shimanouchi, M. Tsuboi and Y. Kyogoku, *Adv. Chem. Phys.*, *7*, 435 (1964).
29 P. C. Kong and T. Theophanides, *Bioinorg. Chem.*, *5*, 51 (1975).
30 G. Y. H. Chu and R. S. Tobias, *J. Am. Chem. Soc.*, *98*, 2641 (1976).
31 P. C. Kong and T. Theophanides, *Inorg. Chem.*, *13*, 1167 (1974).
32 J. Dehand and J. Jordanov, *J. Chem. Soc. Dalton*, 1588 (1977).
33 J. Jordanov and R. J. P. Williams, *Bioinorg. Chem.*, *8*, 77 (1978).
34 P. C. Kong. D. Jyamuremye and F. D. Rochon, *Bioinorg. Chem.*, *6*, 83 (1976).
35 C. L. Hyde and D. J. Darensbourg, *Inorg. Chem.*, *12*, 1075 (1973).
36 R. T. Jernigan, R. A. Brown and G. R. Dobson, *J. Coord. Chem.*, *2*, 47 (1972).
37 U. Reichman, F. Bergmann, D. Lichtenberg and Z. Neiman, *J. Chem. Soc. Perkin I*, 793 (1973).
38 P. Laverture, J. Hubert and A. L. Beauchamp, *Inorg. Chem.*, *15*, 322 (1976).
39 L. M. Twanmoh, H. B. Wood, Jr. and J. S. Driscoll, *J. Heterocycl. Chem.*, *10*, 187 (1973).
40 D. Lichtenberg, F. Bergmann and J. Ringel, *J. Magn. Resonance*, *6*, 600 (1972).
41 G. M. Brown, *Acta Crystallogr. Sect. B*, *25*, 1338 (1969).
42 E. Sletten, J. Sletten and L. H. Jensen, *Acta Crystallogr. Sect. B*, *25*, 1330 (1969).
43 N. Hadjiliadis and T. Theophanides, *Inorg. Chim. Acta*, *15*, 167 (1975).
44 G. Y. H. Chu, S. Mansy, R. E. Duncan and R. S. Tobias, *J. Am. Chem. Soc.*, *100*, 593 (1978).
45 N. Hadjiliadis and T. Theophanides, *Can. J. Spectrosc.*, *22*, 51 (1977).