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Metal Chelates of Dithiocarbazic Acid and Its Derivatives. I. Complexes of Dithiocarbazic Acid and Its *S*-Methyl Ester

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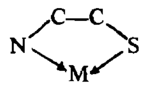
The complexes $Cr(H_2NNHCS_2)_3 \cdot 2H_2O$, $Ni(H_2NNHCS_2)_2 \cdot H_2O$, *and* $M(H_2NNHCS_2)_2$ (*M* = *Pd, Pt, Zn, Cd, Pb*) *have been obtained by the reaction of hydrazinium dithiocarbazate with the appropriate metal salt. Infrared and electronic spectral data indicate that the ligand is coordinated via one nitrogen and one sulphur atom.* S*-Methyldithiocarbazate yields high-spin nickel(II) complexes of two types:* $[Ni(H_2NNHCSSCH_3)_3]X_2$ (*X* = NO_3, *Cl, Br*) *and* $Ni(H_2NNHCSSCH_3)_2X_2$ (*X* = *Cl, NCS*). *Spectral data indicate NS coordination in these compounds. The complexes* $M(H_2NN{=}CSSCH_3)_2$ (*M* = *Ni, Pd, Pt*) *containing deprotonated* S*-methyldithiocarbazate were also isolated; the nickel complex is diamagnetic.*

Introduction

Recently there has been considerable interest in nitrogen-sulphur chelating agents; however, nearly all the metal-ligand systems which have been studied contain the NCCS backbone (I). The analogous NNCS grouping (II) has been less thoroughly investigated. Nevertheless, some of the few examples known have been found to exhibxit biological activity.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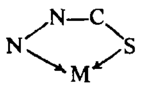
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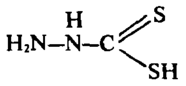
$H_2N{-}NH{-}C({=}S){-}SH$

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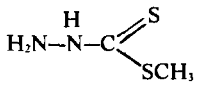

$H_2N{-}NH{-}C({=}S){-}SCH_3$

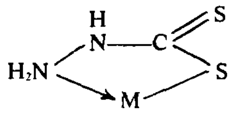
(IV)

We have commenced a study of the metal complexes formed by dithiocarbazic acid (III), *S*-methyldithiocarbazate (IV), and some of their Schiff base derivatives. In this paper we report some metal chelates of the acid (III) and its *S*-methyl ester (IV).

Results and Discussion

Free dithiocarbazic acid, $H_2NNHCSSH$, has only recently been isolated,[1] although its ammonium and hydrazinium salts have long been known.[2] Aqueous solutions of the ammonium salt give precipitates with nickel(II), zinc(II), and cadmium(II). These products were isolated and found to be very impure. It was subsequently found that pure complexes can be obtained by the reaction of hydrazinium dithiocarbazate, $[N_2H_5][H_2NNHCS_2]$ with metal ions in slightly acid aqueous solution. The complexes which were isolated are listed in Table I.

Various metal complexes of dithiocarbazic acid have been reported by other workers.[3-9] The formulations given for these compounds are listed in Table II. These workers have assigned the NS bonded structure (V) to the complexes, although the alternative SS bonded structure (VI) is possible. If SS bonding is present, the complexes would be expected to resemble those of dialkyldithiocarbamates (VII) and dialkyldithiophosphates (VIII),[10,11] which are readily soluble in polar and non-polar organic solvents. The almost complete insolubility of the dithiocarbazate complexes in all solvents suggests that they do not possess the SS bonded structure (VI). However, the insolubility could be due to a polymeric structure.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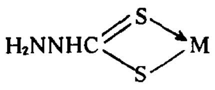
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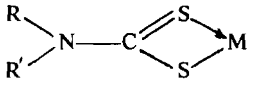
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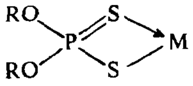
(VIII)

The infrared spectra of all the complexes display a medium to strong band in the region 358-399 cm^{-1}

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Table I. Metal Complexes of Dithiocarbazic Acid

Compound	Colour	ν(M—S) (cm^{-1})	ν(C—N) (cm^{-1})	Analyses % Calcd. Found				
				C	H	N	S	M
$Cr(H_2NNHCS_2)_3 . 2H_2O$	green	374	1470	8.8	3.2	20.5		12.7
				8.8	3.2	19.8		12.5
$Ni(H_2NNHCS_2)_2 . H_2O$	red	374	1485	8.3	2.8	19.25	44.1	20.2
				8.5	2.8	18.8	44.5	20.3
$Pd(H_2NNHCS_2)_2$	yellow	399, 337	1497	7.5	1.9	17.5	40.0	33.2
				8.0	1.7	17.9	40.1	33.8
$Pt(H_2NNHCS_2)_2$ [a]	pale yellow	382, 357	1498	5.9	1.5	13.8		47.7
				6.2	1.4	12.6		47.5
$Pt(H_2NNHCS_2)_2$ [b]	pale yellow	382, 357	1498	5.9	1.5	13.8		47.7
				6.2	1.9	13.3		47.4
$Zn(H_2NNHCS_2)_2$	colourless	373, 364	1485	8.6	2.2	20.0	45.9	23.4
				9.0	2.1	19.7	46.0	23.2
$Cd(H_2NNHCS_2)_2$	colourless	358, 342	1483	7.4	1.8	17.1		34.4
				7.7	1.9	17.0		35.3
$Pb(H_2NNHCS_2)_2$	pale yellow	359, 351	1489	5.7	1.4	13.3	30.4	
				6.1	1.4	13.0	30.5	

[a] Preparation (A); [b] preparation (B).

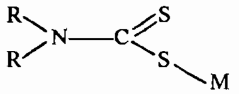
Table II. Metal Complexes of Dithiocarbazic Acid Previously Reported

Complex	Reference
$[Co(H_2NNHCS_2)_2(H_2O)_2] . xH_2O$	5
$[Rh(H_2NNHCS_2)(H_2NNCS_2)(H_2O)_2]$	6
$[Ni(H_2NNHCS_2)_2] . H_2NNHCS_2H$	7
$[Ni(H_2NNHCS_2)_2]$	7
$[Ni(H_2NNHCS_2)_2(H_2O)_2] . 0.5H_2O$	8
$Ni(H_2NNCS_2) . 1.5N_2H_4 . 4H_2O$	6
$Ni_2(H_2NNHCS_2)_2(H_2NNCS_2) . N_2H_4 . 5H_2O$	6
cis—$[Pt(H_2NNHCS_2)_2$	9
trans—$[Pt(H_2NNHCS_2)_2$	9
$Zn(H_2NNCS_2) . 0.5N_2H_4 . 0.75H_2O$	6
$Zn_2(H_2NNHCS_2)_2(H_2NNCS_2) . 5H_2O$	6
$Cd_2(H_2NNHCS_2)_2(H_2NNCS_2) . H_2O$	6
$[Pb(H_2NNHCS_2)_2]$	6

and, in most cases, another, usually weaker, band in the range 337-364 cm^{-1} (see Table I). These bands have been assigned as being essentially metal-sulphur stretching vibrations.

The infrared spectra would be expected to give information concerning the structures of the dithiocarbazate complexes. If NS bonding occurs, the NH_2 stretching frequencies in the complexes should occur at lower frequencies than in the free ligand. Unfortunately there appears to be extensive hydrogen bonding present in the complexes, since the ν(NH_2) bands are broad, complex, and ill-defined.

With *N,N*-dialkyldithiocarbamates the ν(C—N) frequency has been used to distinguish between disulphur chelation (VII) and unidentate sulphur coordination (IX). Where disulphur chelation occurs, ν(C—N)



(IX)

is found within the range 1490-1590 cm^{-1}. With unidentate sulphur coordination the frequency of the C—N stretching vibration has been observed in the range 1460-1490 cm^{-1} and has similar values to those found for the sodium salts of dimethyl and diethyldithiocarbamate.[12,13] A crystal structure determination of hydrazinium dithiocarbazate, $[N_2H_5][H_2NNHCS_2]$ has shown that the NCS_2 group in the dithiocarbazate anion closely resembles that in *N,N*-dialkyldithiocarbamates.[14] Consequently, the criterion, mentioned above, concerning the frequency of ν(C—N) should be applicable to dithiocarbazate complexes. The ν(C—N) frequency for hydrazinium dithiocarbazate occurs at 1500 cm^{-1}. If the metal complexes of dithiocarbazic acid have NS bonded structures, *i.e.* unidentate sulphur coordination (V), then ν(C—N) frequencies below 1500 cm^{-1} would be expected. This is indeed found to be so (see Table I) and is a further indication that NS bonded structures are present. The assignment of the ν(C—N) frequency for the nickel and platinum complexes has been confirmed by the measurement of the infrared spectra of the deuterated complexes. The NH_2 deformation mode occurs at 1586 cm^{-1} for the nickel complex and at 1570 cm^{-1} for the platinum complex. In the spectra of the deuterated complexes this band is absent and δ(ND_2) occurs at 1097 and 1110 cm^{-1} for the nickel and platinum complexes, respectively, while the frequency of ν(C—N) is lowered by about 40 cm^{-1} in each case.

Further evidence of NS bonding is provided by the CS_2 infrared absorption. In dithiocarbamates the asymmetric CS_2 stretching frequency occurs at *ca.* 1000 cm^{-1}. With disulphur chelation a single ν(C=S) is usually found, whereas when unidentate sulphur coordination (IX) occurs, this band is split.[15] The spectra of our dithiocarbazate complexes exhibit strong absorption near 1000 cm^{-1}. In every case this absorption is either split into two bands or has well defined shoulders. This further supports the postulate of unidentate sulphur coordination associated with the NS bonded structure (V). The positions of these bands are unaffected by deuteration in the case of

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the nickel and platinum complexes, as would be expected for ν(CS_2) absorptions. This tends to confirm our assignment of these bands as ν(CS_2) modes.

The isolation of orange-yellow and bright yellow forms of $Pt(H_2NNHCS_2)_2$ has been reported; the former was prepared from *cis*–$[Pt(NH_3)_2Cl_2]$, while the latter was obtained from K_2PtCl_4. It was proposed that these two forms were *cis-trans* isomers, although no supporting physical measurements were made.[9] We were unable to confirm the occurrence of *cis-trans* isomerism for this complex, since the samples which we obtained from both preparative methods (see Experimental Section) had identical infrared spectra and X-ray powder diffraction patterns.

The electronic diffuse reflectance spectrum of the diamagnetic complex $Ni(H_2NNHCS_2]_2 . H_2O$ gives little information about its structure, since it contains a broad envelope with a shoulder at *ca.* 20,000 cm^{-1}; this is the region of absorption usually found for low-spin nickel(II). The spectrum of the chromium complex displays a band at 16,600 cm^{-1} and a shoulder at *ca.* 24,000 cm^{-1}; these bands are assigned to the $^4A_{2g} \rightarrow {}^4T_{2g}$ and $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transitions, respectively (O_h symmetry). The spectrum is significantly different from the spectra of chromium(III) complexes of disulphur chelates such as dithiocarbamates and xanthate, which have the first band at *ca.* 16,000 cm^{-1} but the second at *ca.* 20,000 cm^{-1}.[16-18] If a value of 23,000 cm^{-1} be taken as a lower limit for the energy of the $^4A_{2g} \rightarrow {}^4T_{1g}(F)$ transition, then approximate values for B of 630 cm^{-1} and for $\beta(=B/B_0)$ of 0.7 are obtained for $Cr(H_2NNHCS_2)_3 . 2H_2O$. The disulphur chelates produce a marked lowering of B with values of β of approximtaely 0.45 for chromium(III) complexes.[16] The value of 0.7 obtained for the chromium(III) complex of dithiocarbazic acid, although only approximate, further illustrates the difference between this compound and the SS bonded complexes and suggests the occurrence of unidentate sulphur (*i.e.* NS) coordination.

Both tris- and bis-chelated complexes of nickel were obtained with *S*-methyldithiocarbazate(IV); these are listed in Table III. The tris-chelated complexes are sparingly soluble in dimethylformamide in which they decompose. Both the tris- and the bis-chelated complexes are high-spin and their electronic reflectance spectra are indicative of six-coordinate nickel(II). The $^3A_{2g} \rightarrow {}^3T_{2g}(F)$ transition occurs within the range 11050-11200 cm^{-1} for the tris-chelated complexes and at 10000-10800 cm^{-1} for the bis-chelated complexes, while the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ transition occurs at 17000-17300 cm^{-1} for the tris complexes and at 16100-17600 cm^{-1} for the bis complexes (see Table IV). The infrared spectra display bands in the range 370-347 cm^{-1} (see Table III): these bands have been assigned as essentially ν(Ni–S) modes.

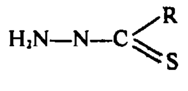
Table III. Metal Complexes of *S*-Methyldithiocarbazate

Compound	Colour	Magnetic moment at 298°K μ (B.M.)	ν(M–S) (cm^{-1})	Analyses % Calcd. Found C	H	N	S	M
$[Ni(H_2NNHCSSCH_3)_3](NO_3)_2$	pale blue	3.09	376, 354	13.1 13.4	3.3 3.5	20.4 19.8		10.7 10.5
$[Ni(H_2NNHCSSCH_3)_3]Cl_2 . H_2O$	pale green	3.00	370	14.0 14.1	3.9 4.0	16.3 16.1		11.4 11.5
$[Ni(H_2NNHCSSCH_3)_3]Br_2$	pale blue	2.99	366, 347	12.3 12.4	3.1 3.3	14.4 13.8		10.0 10.1
$[Ni(H_2NNHCSSCH_3)_2Cl_2] . H_2O$	green	3.11	370, 349	12.3 12.5	3.6 3.0	14.3 14.0		15.0 14.3
$[Ni(H_2NNHCSSCH_3)_2(NCS)_2]$	pale blue	3.09	364, 340	17.2 17.5	2.9 3.2	20.0 19.6		14.0 14.1
$[Ni(H_2NN{=}CSSCH_3)_2]$	buff	diam	418, 321	15.9 15.9	3.4 3.2	18.6 18.2	42.6 42.9	19.5 19.4
$[Pd(H_2NN{=}CSSCH_3)_2]$	yellow	diam	370, 315	13.8 13.8	2.9 3.1	16.1 16.3	36.8 36.6	30.5 30.7
$[Pt(H_2NN{=}CSSCH_3)_2]$	greenish yellow	diam	373, 325	11.0 11.8	2.3 2.5	12.8 12.8		44.6 44.5

Table IV. Electronic Diffuse Reflectance Spectra of Nickel(II) Complexes of *S*-Methyldithiocarbazate

Compound	ν_{max} (cm^{-1}) $^3A_{2g} \rightarrow {}^3T_{2g}(F)$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$
$[Ni(H_2NNHCSSCH_3)_3](NO_3)_2$	11200	17200
$[Ni(H_2NNHCSSCH_3)_3]Cl_2 . H_2O$	11100	17100
$[Ni(H_2NNHCSSCH_3)_3]Br_2$	11100	17200
$[Ni(H_2NNHCSSCH_3)_2Cl_2] . H_2O$	10100	16100
$[Ni(H_2NNHCSSCH_3)_2(NCS)_2]$	10800	17600

As for the complexes of dithiocarbazic acid, both NS and SS bonded structures are possible. However, the former is more likely, especially since the electronic spectra of the tris complexes are very similar to those of the tris-chelated nickel(II) complexes of thiosemicarbazide (X; R = NH_2) and thiocarbazide (X; R = $NHNH_2$) which are known to possess NS bonded structures.[19]



(X)

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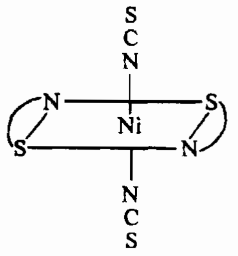
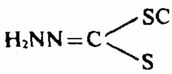


(XI)

The infrared spectrum of the thiocyanato complex $Ni(H_2NNHCSSCH_3)_2(NCS)_2$ display ν(C–N) at 2095 cm^{-1}, indicating the presence of *N*-bonded thiocyanate. The electronic spectrum of this compound displays marked band broadening compared to the spectra of the other complexes. This band symmetry can be explained by the postulate of the *trans*-structure (XI) which would give rise to a weak SS crystal field along one axis and a stronger NN field along the other two axes. A similar structure has been reported for the complex $Ni(H_2NNHCSNH_2)_2(NCS)_2$.[20]

The complex $Ni(H_2NNHCSSCH_3)_2Cl_2$ is high-spin and its electronic spectrum displays narrow symmetric bands unlike the thiosemicarbazide complex $[Ni(H_2NNHCSNH_2)_2]Cl_2$ which is diamagnetic and square-planar.[21] The ligand field strength of *S*-methyldithiocarbazate is similar to that of thiosemicarbazide.[17,19] It is possible that a solid-state effect may lower the donor strength of the ligand in $Ni(H_2NNHCSSCH_3)_2Cl_2$, thereby reducing the tetragonal distortion below that necessary to produce a spin-paired complex. Nevertheless appreciable tetragonal distortion would be expected; this should result in pronounced broadening or splitting of the electronic absorption bands due to the concomitant lowering of symmetry. Since no broadening was observed in the bands of this complex, it seems likely that it has a *cis* configuration. The observed value of 10 D_q — *viz* 10100 cm^{-1} — is in reasonable agreement with the value of 9800 cm^{-1}, calculated from the « average environment » rule for the $NiCl_2N_2S_2$ chromophore by using the values for the $NiCl_6$ chromophore[22] and $[Ni(H_2NNHCSSCH_3)_3]^{2+}$. Although a monomeric *cis* structure is likely, a chloro-bridged structure similar to that found for *cis*–$[Ni(en)_2Cl]_2Cl_2$ cannot be excluded.[23] However, since the complex $Ni(H_2NNHCSSCH_3)_2Cl_2$ is insoluble, no conductivity measurements could be made.

Complexes of the deprotonated ligand (XII) were obtained with nickel(II), palladium(II), and platinum(II) (see Table III) from an aqueous solution of *S*-methyldithiocarbazate containing alkali. The diamagnetism of nickel complex indicates a square-planar configuration: this suggests that the ligand is bound through the terminal nitrogen and thiolo sulphur, since thiols but not thioethers almost invariably cause spin-pairing in complexes of nickel(II).[10]



$H_2NN{=}C\begin{smallmatrix}SCH_3\\ S\end{smallmatrix}$

(XII)

With cobalt(II) and copper(II) salts *S*-methyldithiocarbazate gives insoluble products which slowly decompose, giving off mercaptanlike odours. No pure compounds were isolated.

Several Schiff base derivatives of *S*-methyldithiocarbazate have been found to yield stable, crystalline complexes with a range of metal ions. These complexes will be reported in subsequent parts of this series.

Experimental Section

Analyses. Carbon, hydrogen, and nitrogen were determined by Dr. E. Challen of the Microanalytical Laboratory, University of New South Wales. Sulphur was determined by the Australian Microanalytical Service, Melbourne. Metal analyses were made by standard gravimetric procedures after the complex had been decomposed by heating with a mixture of sulphuric, nitric, and perchloric acids.

Hydrazinium Dithiocarbazate. This compound was prepared by the reaction of hydrazine hydrate with carbon disulphide in alcohol, as reported by Curtius and Heidenreich,[2] and was recrystallized from water.

S-*Methyldithiocarbazate.* This compound was prepared from potassium hydroxide, carbon disulphide, hydrazine hydrate, and methyl iodide by the method of Bähr and Schleitzer.[24] The crude product was dissolved in benzene and reprecipitated by the addition of ligroin; m.p. 80° (Found: C, 19.9; H, 4.9; N, 23.3. Calcd. for $C_2H_6N_2S_2$: C, 19.7; H, 4.95; N, 22.95).

Method of Preparation of Bis(dithiocarbazato) Complexes of Nickel(II), Zinc(II), Cadmium(II), and Lead(II). A solution of hydrazinium dithiocarbazate (0.56 g, 0.004 mole) in water (15 ml) was added dropwise with stirring to a solution of the hydrated metal acetate (0.002 mole) in water (25 ml) containing 5 *M*-acetic acid (1 ml). The stirring was continued for a further 10 min, when the precipitated metal complex was filtered off, washed first with water, then with alcohol, and dried *in vacuo* over potassium hydroxide; yield, 80-85%.

Tris(dithiocarbazato)chromium(III) Dihydrate. A solution of hydrazinium dithiocarbazate (2.0 g, 0.014 mole) in water (25 ml) containing 5 *M*-hydrochloric acid (0.5 ml) was added, with stirring, to a solution of chromium(III) chloride hexahydrate (1.6 g, 0.006 mole) in water (30 ml). After 1 hr the dark green complex was filtered off, washed with water, then with alcohol, and dried *in vacuo* over potassium hydroxide; yield, 1.5 g (62%).

Bis(dithiocarbazato)palladium(II). Potassium chloropalladate(II) (1.0 g) in water (50 ml) was added

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slowly with stirring to a solution of hydrazinium dithiocarbazate (2.0 g) in water (50 ml). The resulting yellow precipitate of the complex was filtered off, washed with 0.5 *M*-acetic acid, then with water, and dried *in vacuo* over potassium hydroxide; yield, 0.4 g (40%).

Bis(dithiocarbazato)platinum(II). Preparation (A). Potassium chloroplatinate(II) (0.5 g) in water (20 ml) was added with stirring to a solution of hydrazinium dithiocarbazate (0.34 g) in water (50 ml). The resulting yellow precipitate was filtered off and dissolved in 0.25 *M*-sodium hydroxide. The addition of 5 *M*-acetic to this solution precipitated the pure complex which was dried at 40° *in vacuo* over potassium hydroxide for 12 hr; yield, 0.3 g (60%).

Preparation (B). Cis-dichlorodiammineplatinum(II) (0.5 g) and hydrazinium dithiocarbazate (3.0 g) were ground together in water (10 ml) in a mortar for 30 min. The resulting paste was kept *in vacuo* over concentrated sulphuric acid for 4 hr. The yellow residue was dissolved in 0.25 *M*-sodium hydroxide (100 ml) and reprecipitated by the addition of 2 *M*-hydrochloric acid dropwise with stirring. The bright yellow complex was filtered off, washed with water, and dried at 60° *in vacuo* over potassium hydroxide; yield, 0.46 g (92%).

Method of Preparation of Tris(S-methyldithiocarbazate)nickel(II) Chloride, Bromide, and Nitrate. The hydrated nickel salt (0.0025 mole) in alcohol (40 ml) was added to a hot solution of *S*-methyldithiocarbazate (1.0 g, 0.0082 mole) in alcohol (25 ml) containing 5 *M*-mineral acid (1 ml). The solution, on cooling, deposited crystals of the complex; these were filtered off, washed with alcohol, and dried *in vacuo* over phosphorus pentoxide; yield, 75-85%.

Dichlorobis(S-methyldithiocarbazate)nickel(II) Monohydrate. S-Methyldithiocarbazate (0.5 g) in hot alcohol (10 ml) was added to a solution of nickel chloride hexahydrate (2 g) in hot alcohol (40 ml). The mixture was cooled and the green crystalline complex was filtered off, washed with alcohol, and dried *in vacuo* over phosphorus pentoxide; yield, 0.74 g (92%).

Dithiocyanatobis(S-methyldithiocarbazate)nickel(II). *S*-Methyldithiocarbazate (0.5 g) in hot alcohol (10 ml) was added to a solution of nickel thiocyanate (1 g) in hot 90% alcohol (100 ml). The mixture was cooled and the pale blue complex was filtered off, washed with alcohol, and dried *in vacuo* over phosphorus pentoxide; yield, 0.8 g (93%).

Bis(S-methyldithiocarbazato)palladium(II). Potassium chloropalladate(II) (0.5 g) in water (20 ml) was added to the filtered solution obtained by dissolving *S*-methyldithiocarbazate (0.4 g) in water (20 ml) containing potassium hydroxide (0.12 g). The resulting yellow precipitate of the complex was filtered off, washed with water, and dried *in vacuo* over phosphorus pentoxide; yield, 0.4 g (75%).

Bis(S-methyldithiocarbazato)platinum(II). The platinum complex was prepared from potassium chloroplatinate(II) in a similar manner to that described for the palladium complex; yield, 0.6 g (85%).

Bis (S-methyldithiocarbazato)nickel(II). S-Methyldithiocarbazate (1.5 g) was added to a solution of potassium hydroxide (0.45 g) in water (20 ml). The solution was stirred for 5 min and then filtered. To the filtrate a solution of nickel chloride hexahydrate (0.95 g) in water 10 ml) was added. The resulting beige precipitate was filtered off, washed several times with water, and dried *in vacuo* over phosphorus pentoxide at 60° for 12 hr; yield, 1.2 g (95%).

Preparation of Deuterated Complexes. Hydrazium dithiocarbazate (9.25 g) was dissolved in deuterium oxide (5 ml). The solution was kept standing in a stoppered flask for 3 hr before use. Deuterated acetic acid was prepared by refluxing acetic anhydride with the requisite amount of deuterium oxide; this was diluted further with deuterium oxide. The metal salts were dissolved in deuterium oxide and the preparations were carried out as described above, preparation (A) being used for the platinum complex.

Spectral Measurements. The electronic diffuse reflectance spectra were measured on a Zeiss PMQII spectrophotometer from the sample spread on filter paper. The infrared spctra were obtained from nujol or halocarbon mulls on a Perkin-Elmer 337 spectrophotometer for the range 4000-400 cm^{-1} and on a Perkin-Elmer 521 spectrophotometer below 400 cm^{-1}.

X-Ray Diffraction Data. The X-ray powder diffraction paterns were obtained with CuK_α radiation on a Philips PW1010 generator with a Philips camera of radius 57.3 mm.

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