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Metal Chelates of Dithiocarbazic Acid and Its Derivatives. VIII. Metal Ion Induced Rearrangement of Some 1,3,4-Thiadiazoline-2-thiones Derived from Dithiocarbazic Acid

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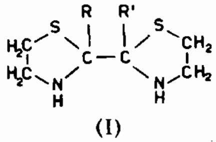
Received November 8, 1972

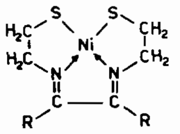
In the presence of certain metal salts 3,3,5-trimethyl-1,3,4-thiadiazolidine-2-thione, 5,5-dimethyl-1,3,4-thiadiazolidine-2-thione, and 5-(2-pyridyl)-1,3,4-thiadiazolidine-2-thione undergo rearrangement to yield neutral metal chelates of the tautomeric Schiff bases, respectively, α-N-methyl-β-N-isopropylidentithiocarbazate (N-Me-SH) isopropylidentithiocarbazate (N-SH), and β-N-(2-pyridyl)methylendithiocarbazate (N-N-SH). The compounds isolated were M(NMe-S)$_2$ (M = Ni, Cu, Pd), M(N-S)$_2$ (M = Ni, Pd), Co(N-S)$_3$. H$_2$O, and Ni-(N-N-S).

Introduction

The condensation of 2-aminoethanethiol with an aldehyde does not give a Schiff base but a thiazoline. Similarly, 2-aminobenzenethiol forms a benzothiazoline.[1] α-Diketones react with 2-aminoethanethiol to yield a bis-thiazolidinyl (I) as the main product. However, in the presence of nickel ions α-dicktones react with 2-aminoethanethiol to yield nickel complexes (II) of the corresponding Schiff bases in good yield.[2]

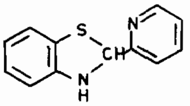


(I)



(II)

Pyridine-2-aldehyde reacts with 2-aminobenzenethiol to yield 2-(2-pyridyl) benzothiazoline (III) instead of the expected Schiff base (IV). But in the presence of metal ions the benzotiazoline (III) rearranges to the Schiff base (IV) and yields intensely coloured metal complexes of (IV).[3]



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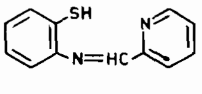
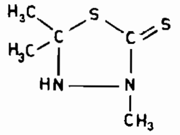


(IV)

These and other metal-ion induced reactions involving the formation of metal complexes of sulphur ligands have been reviewed by Lindoy.[1] In this paper some metal-ion induced rearrangements of the dithiocarbazic acid derivatives, 3,5,5-trimethyl-1,3,4-thiadiazoline-2-thione (V), 5,5-dimethyl-1,3,4-thiadiazoline-2-thione (VI), and 5-2-pyridyl)-1,3,4,-thiadiazoline-2-thione (VII) are discussed.



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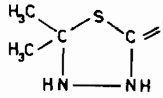

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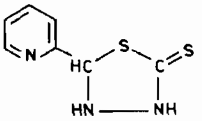
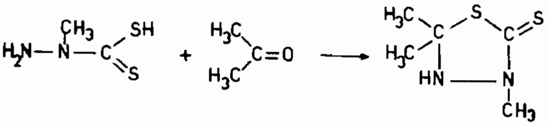


(VII)

Results and Discussion

The condensation of *N*-methyldithiocarbazic acid with acetone in alcohol solution yields a white crystalline product which was considered[4] to be 3,5,5-trimethyl-1,3,4-thiadiazolidine-2-thione (V) rather than the Schiff base α-*N*-methyl-β-*N*-isopropylidendithiocarbazic acid (VIII; NMe-SH). The infrared spectrum of the product obtained by the condensation of *N*-methyldithiocarbazic acid with acetone shows no band which can be assigned to the S-H stretching mode of the Schiff base form (VIII) but the spectrum does display a band of medium intensity at 3122



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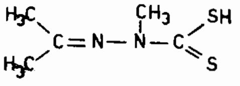

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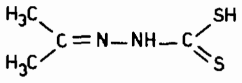

(IX)

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[1] L.F. Lindoy, *Coord. Chem. Rev.*, *4*, 41 (1969).
[2] M.C. Thompson and D.H. Busch, *J. Amer. Chem. Soc.*, *84*, 1762 (1962), *86*, 213 (1964).
[3] L.F. Lindoy and S.E. Livingstone, *Inorg. Chim. Acta*, *1*, 365 (1967).
[4] F.C. Heugebaert and J.F. Willems, *Tetrahedron*, *22*, 913 (1966).

Table I. Metal Complexes of the Schiff Bases.

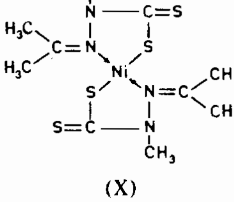
Prepared from thiadiazolidine	Compound	Colour	Mol. conduct. Λ_{1000} in $MeNO_2$ at 25° (ohm^{-1} cm^2mole^{-1})
V	$Ni(NMe\text{-}S)_2$	brownish-green	0
V	$Cu(NMe\text{-}S)_2$	brown	0
V	$Pd(NMe\text{-}S)_2 . 2H_2O$	orange	i.s.
VI	$Ni(N\text{-}S)_2$	brownish-green	1.0
VI	$Co(N\text{-}S)_3 . H_2O$	green	0
VI	$Pd(N\text{-}S)_2$	orange	i.s.
VII	$Ni(N\text{-}N\text{-}S)$	red	4.0

i.s. = insufficient solubility.

cm^{-1} and a weaker band at 3170 cm^{-1}; these bands are assigned as ν(N-H) of the thiazolidine form (V).

Similarly hydrazinium dithiocarbazate, $[N_2H_5][H_2NNHCS_2]$, reacts with acetone to yield 5,5-dimethyl-1,3,4-thiadiazolidine-2-thione (VI) and not the Schiff base *N*-isopropylidendithiocarbazic acid (IX; N-SH). The infrared spectrum shows no ν(S-H) absorption.

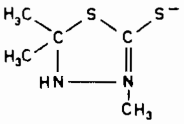
A solution of (V) in alcohol reacts with nickel acetate to yield a brownish-green diamagnetic complex of stoicheiometry $Ni(C_5H_9N_2S_2)_2$. The similar copper complex and a palladium complex $Pd(C_5H_9N_2S_2)_2$ were also isolated. The conductivities of these and the other metal complexes described in this paper are listed in Table I. The diamagnetism of the nickel complex suggests that it is coordinated by the thiolo sulphur of the Schiff base form (VIII), since thiols usually cause spin-pairing in nickel complexes.[5] The electronic spectrum of the crystalline nickel complex is typical of low-spin square-planar nickel(II). The first spin-allowed transition ν_1 occurs at 18,200 cm^{-1}, which is close to the frequency of ν_1 for the thiosemicarbazide complexes of nickel, whose chromophore has been established as NiN_2S_2.[6] The conductivity, diamagnetism, and electronic spectrum suggest that the complex has the structure (X) in which the nickel atom is coordinated via the β-nitrogen and the thiolo sulphur atoms of the Schiff base. The infrared spectrum shows a band of medium intensity at 1639 cm^{-1} which is assigned as $\nu(C=N)$ of the Schiff base. This band is absent from the spectrum of the thiadiazolidine (V).



(X)

Copper acetate reacts with the thiadiazoline (V) to give the brown copper complex which has a magnetic moment of 1.90 B.M. The infrared spectra of the copper and the palladium complexes display $\nu(C=N)$ at 1640 cm^{-1}, indicating that in both complexes, the ligand is coordinated in the Schiff base form.

The thiadiazoline (VI) reacts with nickel perchlorate in alcohol solution to give the brownish-green complex $Ni(C_4H_7N_2S_2)_2$. The infrared spectrum of the complex shows $\nu(C=N)$ at 1620 cm^{-1}; however, the occurrence of $\nu(C=N)$ in the spectrum, unlike in the case of $Ni(MeN\text{-}S)_2$, cannot be taken as proof of the presence of the ligand in the Schiff base form (IX), since the thiadiazoline (VI) when deprotonated can exist in the tautomeric form (XI) which would display $\nu(C=N)$ in its infrared spectrum. The solid state electronic spectrum is virtually identical with that of $Ni(MeN\text{-}S)_2$, suggesting that the thiadiazoline (VI) has rearranged in the presence of nickel ions to give the complex $Ni(N\text{-}S)_2$ in which the ligand is present in the Schiff base form (IX). Indeed it is difficult to suggest a structure for the complex in which the thiadiazoline (VI) can act as a uninegatively charged NS ligand. Therefore it is reasonable to assume that the ligand is present in the Schiff base form.



(XI)

The complex $Ni(N\text{-}S)_2$ was obtained by two other methods: (i) by heating a solution of nickel nitrate, acetone, and hydrazinium dithiocarbazate in alcohol; and (ii) by heating bis(dithiocarbazato)nickel(II) monohydrate[7] in a mixture of acetone and alcohol at the reflux for 15 hours (see Experimental Section). The products from both these preparations had infrared spectra identical with that of the complex prepared from the thiadiazoline (VI). It has been suggested that there is little evidence to indicate that amine ligands will undergo Schiff-base condensation reactions whilst coordinated.[8,9] If this is so, then the reaction of bis(dithiocarbazato)nickel(II) with acetone must involve a small dissociation of the complex to yield the free ligand in the reaction mixture. However, the possibility of other less obvious mechanisms cannot be discounted. The reactions involving the nickel complex are summarized in Scheme I.

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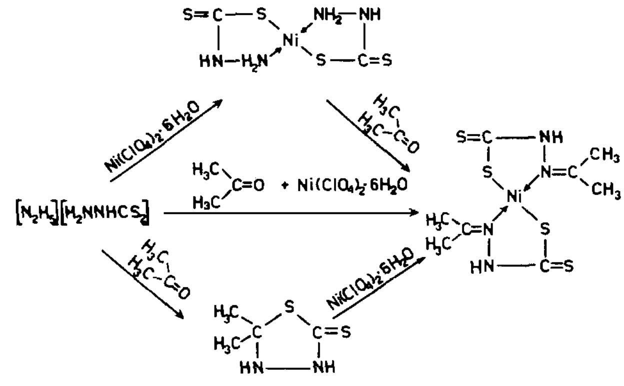
(5) S.E. Livingstone, *Quart. Rev.*, *19*, 386 (1965).

(6) R. Gronbaek and S.E. Rasmussen, *Acta Chem. Scand.*, *16*, 2325 (1962).

(7) M. Akbar Ali, S.E. Livingstone, and D.J. Phillips, *Inorg. Chim. Acta*, *5*, 119 (1971).

(8) D.H. Busch, *Advan. Chem. Ser.*, *37*, 1 (1963).

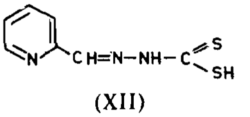
(9) D. St. C. Black and E. Markham, *Rev. Pure and App. Chem.* (Australia), *15*, 109 (1965).



Scheme I.

If cobalt(II) thiocyanate is added to a solution of the thiadiazoline (VI), the green, diamagnetic cobalt (III) complex Co(N-S)$_3$. H$_2$O is obtained. The isolation of a cobalt(III) complex from a cobalt(II) solution is indicative of mercapto sulphur coordination, since similar rapid oxidation of cobalt(II) to give a cobalt(III) complex occurs in the presence of ligands containing thiolo groups such as monothio-β-diketones[10] and *S*-methyl-β-*N*-(2-pyridyl)methylendithiocarbazate.[11] A palladium(II) complex Pd(S-N)$_2$ was also isolated. The ν(C=N) band occurs at 1620 and 1630 cm^{-1} in the spectra of the cobalt and palladium complexes, respectively.

5-(2-Pyridyl)-1,3,4-thiadiazolidine-2-thione (VII) reacts with nickel acetate in alcohol to give a red complex Ni(C$_7$H$_6$N$_3$S$_2$)$_2$. H$_2$O, which is virtually a non-electrolyte in nitromethane (Λ_{1000}, 4 ohm^{-1} cm^2 mole^{-1}). Its magnetic moment (3.10 B.M.) is typical of high-spin octahedral nickel(II). It is very likely that in the presence of nickel ions the thiadiazolidine (VII) rearranges to the Schiff base (XII; N-N-SH) with the concomitant formation of an octahedral complex in which the nickel atom is bound through the pyridine nitrogen, the β-nitrogen and the thiolo sulphur. A similar rearrangement of 2-(2-pyridyl)benzothiazoline (III) occurs in the presence of nickel acetate to give a paramagnetic octahedral complex of the Schiff base *N*-2-mercaptophenyl-2'-pyridylmethylenimine (IV).[12]



(XII)

Experimental Section

Unless otherwise stated all the compounds, after filtration, were washed with alcohol and dried *in vacuo* over phosphorus pentoxide.

3,5,5-Trimethyl-1,3,4-thiadiazolidine-2-thione. The method of preparation of this compound has been reported by Heugebaert and Willems.[4] However, in the present investigation a slightly different procedure was used.

Carbon disulphide (20 g) was added, with vigorous stirring, to a solution of methylhydrazine (20 g) in water (50 ml). The stirring was continued until a completely clear solution was obtained. Acetone (50 ml) was added and the solution was kept overnight at room temperature. Water (200 ml) was added and the white crystals which had had formed were filtered off and recrystallized from alcohol to give the pure compound; yield, 15 g; m.p. 78°, lit.[4] 78-79° (Found: C, 37.0; H, 6.2; N, 16.7. C$_5$H$_{10}$N$_2$S$_2$ requires C, 37.1; H, 6.2; N, 17.3%).

5,5-Dimethyl-1,3,4-thiadiazolidine-2-thione. This compound was prepared by a slightly different method from that reported by Heugebaert and Willems.[4]

Acetone (10 ml) was added to a solution containing hydrazinium dithiocarbazate (5.0 g) in water (100 ml). The white crystalline material which formed was filtered off, washed with a 1:1 mixture of alcohol and ligroin and dried; yield, 3.5 g; m.p. 118°, lit.[4] 120-125°. (Found: C, 32.3; H, 5.4; N, 18.7. C$_4$H$_8$N$_2$S$_2$ requires C, 32.4; H, 5.4; N, 18.9%).

5-(2-Pyridyl)-1,3,4-thiadiazolidine-2-thione. This compound was prepared from pyridine-2-aldehyde hydrazone and carbon disulphide according to the method of Heugebaert and Willems;[4] m.p. 117-124°, lit.[4] 118-125°.

Bis(α-N-methyl-β-N-isopropylidendithiocarbazato)nickel(II). Nickel acetate tetrahydrate (1.5 g) was heated in alcohol (80 ml) for 10 min. The mixture was filtered into a hot solution of 3,5,5-trimethyl-1,3,4-thiadiazolidine-2-thione (2.0 g) in alcohol (20 ml). After the solution had been heated for 3 min, it was left standing for 1 hr, whereupon beautiful brownish-green crystals of the complex formed; yield, 1.1 g. (Found: C, 31.7; H, 4.7; N, 14.5; S, 33.0; Ni, 15.5. C$_{10}$H$_{18}$NiN$_4$S$_4$ requires C, 31.5; H, 4.8; N, 14.7; S, 32.8; Ni, 15.4%).

Bis(α-N-methyl-β-N-isopropylidendithiocarbazato)-copper(II). Cupric acetate monohydrate (1.2 g) was heated in alcohol (80 ml) for 10 min. and then the mixture was filtered. The filtrate was added to a solution of 3,3,5-trimethyl-1,3,4-thiadiazolidine-2-thione (2.0 g) in alcohol (20 ml). On being heated on the water bath for 3 min, the solution turned brown, and slowly deposited brown crystals of the copper complex; yield, 1.5 g. (Found: C, 31.5; H, 4.8; N, 13.9; S, 33.1; Cu, 16.4. C$_{10}$H$_{18}$CuN$_4$S$_4$ requires C, 31.1; H, 4.7; N, 14.5; S, 33.2; Cu, 16.5%).

Bis(α-N-methyl-β-N-isopropylidendithiocarbazato)-palladium(II) Dihydrate. Potassium tetrachloropalladate(II) (1.04 g) in hot water (20 ml) was added to a solution of 3,5,5-trimethyl-1,3,4-thiadiazolidine-2-thione (1.0 g) in acetone (25 ml). The mixture was heated on the steam bath for 2 min, then allowed to cool, whereupon orange crystals of the complex formed; yield, 1.5 g. (Found: C, 25.6; H, 3.9; N, 11.9; Pd, 23.3. C$_{10}$H$_{22}$N$_4$O$_2$PdS$_4$ requires C, 25.8; H, 4.8; N, 12.05; Pd, 22.9%).

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[10] S.H.H. Chaston and S.E. Livingstone, *Austral. J. Chem.*, *20*, 1065 (1967).

[11] M. Akbar Ali, S.E. Livingstone, and D.J. Phillips, *Inorg. Chim. Acta*, *5*, 493 (1971).

[12] L.F. Lindoy and S.E. Livingstone, *Inorg. Chem.*, *7*, 1149 (1968).

Bis(dithiocarbazato)nickel(II) Monohydrate. This was prepared as previously described.[7]

Preparation of Bis(isopropylidendithiocarbazato)nickel(II). Preparation (A). A solution of nickel perchlorate hexahydrate (1.0 g) in a mixture of alcohol (30 ml) and 2,2-dimethoxypropane (5 ml) was added to a solution of 5,5-dimethyl-1,3,4-thiadiazolidine-2-thione (1.0 g) in a hot mixture of alcohol (30 ml) and acetone (2 ml). After being heated on the steam bath for 3 min, the solution was cooled, whereupon brownish-green crystals of the complex resulted; yield, 0.5 g. (Found: C, 27.3; H, 4.1; N, 15.3; S, 35.2; Ni, 16.5 $C_8H_{14}N_4NiS_4$ requires C, 27.2; H, 4.0; N, 15.9; S, 36.3; Ni, 16.6%).

Preparation (B). The above compound was also prepared by mixing nickel nitrate, acetone, and hydrazinium dithiocarbazate *in situ* according to the following method; nickel perchlorate hexahydrate (2.9 g) was heated at the reflux in a mixture of alcohol (50 ml), 2,2-dimethoxypropane (10 ml), and acetone (10 ml) for 30 min. Hydrazinium dithiocarbazate[7] (2.8 g) was added, whereupon a red precipitate appeared, and then redissolved when the reaction mixture was heated for 15 min. The dark brown solution slowly deposited brownish-green crystals upon cooling; these were filtered off; yield, 1.2 g. (Found: C, 27.6; H, 4.0; N, 15.7; Ni, 16.5. $C_8H_{14}N_4NiS_4$ requires C, 27.2; H, 4.0: N, 15.9; Ni, 17.1%).

Preparation (C). The above compound was also prepared by the condensation of acetone directly with bis(dithiocarbazato)nickel(II) monohydrate according to the following method: finely ground bis(dithiocarbazato)nickel(II) monohydrate[7] (1.0 g) was refluxed in a mixture of acetone (150 ml) and alcohol (50 ml) for 15 hr. The light brown mixture was filtered hot and the filtrate was concentrated to 20 ml, whereupon brownis-green crystals of the complex were obtained; yield, 0.2 g. (Found: C, 27.9; H, 4.5; N, 15.2; Ni, 16.3. $C_8H_{14}N_4NiS_4$ requires C, 27.2; H, 4.0; N, 15.9; Ni, 16.6%).

Tris(isopropylidendithiocarbazato)cobalt(III) Monohydrate. Cobalt thiocyanate (1.0 g) in alcohol (100 ml) was added to a solution of 5,5-dimethyl-1,3,4-thiadiazolidine-2-thione (1.0 g) in hot alcohol (50 ml). The mixture was heated on the steam bath for 3 min and then allowed to cool. After 1 hr the green powder which had formed was filtered off; yield, 0.6 g. (Found: C, 28.0; H, 4.35; N, 16.1; S, 36.7. $C_{12}H_{23}CoN_6OS_5$ requires C, 27.8; H, 4.5; N, 16.2; S, 37.1%).

Bis(isopropylidendithiocarbazato)palladium(II). Potassium tetrachloropalladate(II) in hot water (20 ml) was added to a boiling solution of 5,5-dimethyl-1,3,4-thiadiazolidine-2-thione (1.0 g) in acetone (10 ml). After being heated on the steam bath for 2 min, the mixture yielded orange crystals which were filtered off, washed first with water, and then with acetone; yield, 1.0 g. (Found: C, 24.2; H, 3.5; N, 13.5; S, 31.6; Pd, 26.5. $C_8H_{14}N_4PdS_4$ requires C, 24.0; H, 3.5; N, 14.0; S, 32.0; Pd, 26.5%).

Bis{β-N-(2-pyridyl)methylendithiocarbazato}nickel(II) Monohydrate. Nickel acetate tetrahydrate (0.5 g) was heated in boiling alcohol (100 ml) and the mixture was filtered hot. The filtrate was added to a solution of 5-(2-pyridyl)-1,3,4,-thiadiazolidine-2-thione (1.0 g) in hot alcohol (100 ml). The solution was heated on the steam bath for 15 min, cooled for 1 hr, and the pale red precipitate which had deposited was collected; yield, 0.5 g. (Found: C, 35.8; H, 3.0; N, 18.0; Ni, 12.4. $C_{14}H_{14}N_6NiOS_4$ requires C, 35.8; H, 3.0; N,17.9; Ni, 12.5%).