Conformational Studies of some Potentially Bidentate Thiosemicarbazones and Related Complexes of Zinc(II)

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N.m.r. spectra of some potentially bidentate thiosemicarbazones, $NR^3H{\cdot}CS{\cdot}NH{\cdot}N{:}CR^2R^1$ (L: R^1,R^2 = H, Me, Ph, or $R^1R^2 = C_6H_{11}$; R^3 = H or Ph), and their complexes $[ZnCl_2L]$ or $[ZnCl_2L_2]$ have been measured. The results are compared with semiempirical CNDO/2 total-energy calculations. Only one conformer, containing an intramolecular hydrogen bond, is present in solution. All the zinc(II) complexes are tetrahedral. The possible formation of complexes in which the ligand is bidentate is discussed.

THE synthesis and physicochemical characterisation of transition-metal complexes with thiosemicarbazone-type ligands is being undertaken in our laboratory. The interest in these ligands is connected with their flexibility which leads to extremely variable behaviour in their reactions with transition and non-transition metals.

Many of these thiosemicarbazones, and especially potentially tridentate ones, show some biological activity which depends on the parent carbonyl compound.[1-3] Recently, several papers have appeared[4] on the *X*-ray structures of these ligands and a few of their complexes, in an attempt to find a connection between the crystal structure and the biological activity of these compounds.

We report an n.m.r. study in solution of some thiosemicarbazones and their complexes with Zn^{II}.

EXPERIMENTAL

The starting carbonyl compounds and the thiosemicarbazide were Merck reagent-grade products; 4-phenylthiosemicarbazide was a K and K reagent and $ZnCl_2$ an Erba RP product. Thiosemicarbazones were prepared following the procedures of Sah and Daniels.[5] The crude products were recrystallised several times from water–ethanol mixtures.

Elemental analyses are reported in Table 1. The melting points (Table 1) were determined with a Kofler apparatus and are uncorrected. The measured values agree well with those reported in the literature.[5] The zinc complexes were prepared by heating anhydrous $ZnCl_2$ and the ligand (1 : 1 or 1 : 2 mole ratio) under reflux in absolute ethanol for 1 h as reported by Ablov and Gerbeleu.[6] Cooling the reaction mixture gave the complexes in crystalline form. The products were recrystallised from absolute ethanol. The

TABLE 1

Analytical data for the thiosemicarbazones

		Analysis (%)						
		Found			Calc.			
Compound	Formula	C	N	H	C	N	H	M.p. (θ_c/°C)
Acetone thiosemicarbazone, (I)	$C_4H_9N_3S$	36.5	32.15	6.95	36.65	32.05	6.85	181—183
Benzaldehyde thiosemicarbazone, (II)	$C_8H_9N_3S$	53.6	23.65	5.05	53.65	23.45	5.00	159—161
Acetophenone thiosemicarbazone, (III)	$C_9H_{11}N_3S$	55.85	21.9	5.65	55.95	21.75	5.70	118—120
Cyclohexanone thiosemicarbazone, (IV)	$C_7H_{13}N_3S$	49.4	24.65	7.80	49.1	24.55	7.60	159—161
Acetone 4-phenyl-3-thiosemicarbazone, (V)	$C_{10}H_{13}N_3S$	58.25	19.2	6.50	58.0	20.3	6.30	126—128

TABLE 2

Analytical data for the zinc complexes

			Analysis (%)					
Complex	Formula		Zn	C	N	H	Cl	M.p. (θ_c/°C)
(Acetone thiosemicarbazone)-dichlorozinc(II), (VI)	$[ZnCl_2(C_4H_9N_3S)]$	calc:	24.45	17.95	15.7	3.35	26.5	160—162
		found:	24.5	17.95	15.8	3.50	25.4	
Bis(acetone thiosemicarbazone)-dichlorozinc(II), (VII)	$[ZnCl_2(C_4H_9N_3S)_2]$	calc:	16.4	24.1	21.1	4.50	17.8	240—242
		found:	16.25	24.15	21.25	4.65	17.9	
Bis(benzaldehyde thiosemicarbazone)-dichlorozinc(II), (VIII)	$[ZnCl_2(C_8H_9N_3S)_2]$	calc.:	13.2	38.85	17.0	3.65		
		found:	13.2	38.8	16.95	3.60		
Bis(acetophenone thiosemicarbazone)-dichlorozinc(II), (IX)	$[ZnCl_2(C_9H_{11}N_3S)_2]$	calc.:	12.5	41.35	16.1	4.20		
		found:	12.5	41.55	16.3	4.25		
Dichloro(cyclohexanone thiosemicarbazone)zinc(II), (X)	$[ZnCl_2(C_7H_{13}N_3S)]$	calc.:	21.25	27.35	13.65	4.25		237—240
		found:	21.6	27.5	13.15	4.25		
Bis(acetone 4-phenyl-3-thiosemicarbazone)dichlorozinc(II), (XI)	$[ZnCl_2(C_{10}H_{13}N_3S)_2]$	calc.:	11.9	43.6	15.25	4.70		
		found:	11.9	43.5	15.05	4.90		

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[1] F. A. French and E. J. Blanz, jun., *J. Medicin. Chem.*, 1966, **9**, 585.

[2] R. E. Hagenbach and H. Gysui, *Experientia*, 1952, **8**, 184.

[3] E. J. Blanz, jun., and F. A. French, *Cancer Res.*, 1968, **28**, 2419.

[4] G. J. Palenik, D. F. Rendle, and W. S. Carther, *Acta Cryst.* 1974, **B30**, 2390 and refs. therein.

[5] P. T. T. Sah and T. C. Daniels, *Rec. Trav. chim.*, 1950, **69**, 1545.

reaction of acetone thiosemicarbazone with $ZnCl_2$ yielded two products: [$ZnCl_2L$], previously prepared by Ablov and Gerbeleu [6] and characterised in the solid state by Mathew and Palenik; [7] and [$ZnCl_2L_2$], not reported previously. The elemental analyses and m.p.s of the complexes are shown in Table 2.

The zinc content was determined by titrimetric analysis with ethylenediaminetetra-acetic acid using Xylenol Orange as indicator; [8] potentiometric titration with Ag[NO_3] was used to determine the chloride content.[9] The n.m.r. spectra were recorded at 90 MHz (Bruker HX-90 spectrometer), $SiMe_4$ being used as internal standard and for field stabilization. A Bruker B-ST 100/700 accessory equipped with a thermocouple was used for variable-temperature measurements. The deuteriated solvents were Merck UVASOL reagents.

The molecular-orbital (m.o.) calculations were made at the Centro di Calcolo of the University of Rome. The semiempirical CNDO/2 method was employed, making use of a modified QCPE program.* Bond lengths and angles for the molecules investigated are from refs. 4 and 10 and were kept constant for the different conformations.

A Kholrausch SIS-Halosis FA_2-type bridge was used for the conductivity measurements.

TABLE 3

Chemical shifts ^{a} of *N*-bonded protons of some thiosemicarbazones in $CDCl_3$

Compound	(I)		(II)		(III)		(IV)		(V)	
T/K	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H
318			9.64	*b*, 6.39	8.73	*b*, 6.29 ± 0.06	8.81	7.18 ± 0.04, 6.50 ± 0.05	8.45	9.27
303	8.52	7.20 ± 0.04 ^{c} 6.37 ± 0.04	9.88	*b*, 6.45	8.77	*b*, 6.39 ± 0.06	8.92	7.28, 6.59	8.55	9.30
288	8.51	7.22 ± 0.04,^{c} 6.33 ± 0.04	10.11	*b*, 6.52	8.82	*b*, 6.49 ± 0.03	8.98	7.30, 6.67	8.58	9.31
273	8.56	7.27 ± 0.04,^{c} 6.37 ± 0.04	10.38	*b*, 6.64	8.85	*b*, 6.59	9.06	7.31, 6.77	8.60	9.31
258	8.56	7.30 ± 0.04,^{c} 6.42	10.67	*b*, 6.72	8.89	*b*, 6.68	9.13	7.34, 6.86	8.65	9.33
243	8.62	7.32 ± 0.03,^{c} 6.54	10.93	*ca.* 7.4,^{d} 6.81 ^{e}	8.93	*b*, 6.78	9.20	7.36, 6.98	8.72	9.34
228	8.72	7.37, 6.74 ^{e}	11.15	*ca.* 7.4,^{d} 6.91	8.97	*b*, 6.88 ^{e}	9.29	7.38, 7.11 ^{f}	8.77	9.35
213	8.81	7.40, 6.98	11.38	*ca.* 7.4,^{d} 7.05	9.02	*b*, 6.97	9.42	7.42, 7.29	8.81	9.36

^{a} δ ±0.02 p.p.m. from $SiMe_4$, unless otherwise indicated. ^{b} Obscured by aromatic protons. ^{c} Interference from $CHCl_3$. ^{d} Shoulder. ^{e} *J*(*gem*) 3.5 ± 0.5 Hz. ^{f} *J* (*gem*) 4.3 ± 0.2 Hz.

TABLE 4

Chemical shifts ^{a} of some thiosemicarbazones in [$^2H_6$]acetone

Compound	(I)		(II)		(III)		(IV)		(V)	
T/K	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H
318							9.08	*ca.* 7.4,^{b} *ca.* 7.2 ^{b}	9.04 ± 0.04	9.64 ± 0.04
303	9.00	7.33 ± 0.08	10.61	*c*, 7.58 ± 0.04	9.33	*c*, 7.53 ± 0.04 ^{e}	9.16	7.46 ± 0.05,^{b} 7.17 ± 0.05 ^{b}	9.13	9.70
288	9.02	7.42 ± 0.08	10.67	*c*, *c*	9.41	*c*, 7.64 ± 0.06	9.24	7.53 ± 0.04,^{b} 7.33 ± 0.05 ^{b}	9.23	9.79
273			10.77	8.04, *c*	9.48	8.04,^{c} *ca.* 7.76 ± 0.03	9.33	7.62 ± 0.03,^{b} 7.42 ± 0.04 ^{b}	9.32	9.83
258	9.18	7.63 ± 0.04	10.88	8.13, *c*	9.54	8.08, *c*	9.44	7.70, 7.57	9.42	9.91
243			10.98	8.22, 8.02	9.67	8.23, *c*	9.52	7.80, 7.69	9.52	9.99
228	9.36	7.87	11.09	8.40, 8.16	9.72	8.29, 8.13	9.61	7.90, 7.81	9.61	10.06
213	9.43	7.97	11.21	8.46, 8.27 ^{d}	9.82	8.41, 8.29 ^{e}	9.70	7.99, 7.94	9.71	10.16
198	9.53	8.09	11.32	8.57, 8.41	9.91	8.50, 8.41			9.81	10.24
183	9.63	8.23	11.42	8.66, 8.51	10.00	8.59, 8.52			9.90	10.32

^{a} δ ±0.02 p.p.m. from $SiMe_4$, unless otherwise indicated. ^{b} Overlapping. ^{c} Obscured by aromatic protons. ^{d} *J*(*gem*) 2.2 ± 0.5 Hz. ^{e} *J*(*gem*) 2.5 ± 0.5 Hz.

TABLE 5

Chemical shifts * of *N*-bonded protons of zinc(II) complexes with thiosemicarbazones in [$^2H_6$]acetone

Compound	(VI)		(VII)		(VIII)		(IX)		(X)		(XI)	
T/K	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H	N(2)-H	N(4)-H
303	10.90	, 8.28 ± 0.06	10.18	, 8.18	11.38	8.58,	10.33	8.42	10.9	8.17	10.03	10.03
288	10.98	8.40 ± 0.06, 8.11 ± 0.06	10.22	, 8.26 ± 0.03	11.46	8.61,	10.40	8.51			10.04	10.13
273	11.05	8.80 ± 0.04, 7.79 ± 0.04	10.27	, 8.36	11.53	8.68,	10.44	8.60			10.11	10.23
258	11.20	8.94, 7.93	10.30	8.49, 8.42	11.59	8.80, 8.76	10.51	8.70			10.18	10.37
243	11.30	9.03, 7.95	10.33	8.60, 8.52	11.68	8.87, 8.79	10.56	8.82			10.22	10.47
228	11.38	9.09, 7.96	10.37	8.72, 8.66	11.74	8.99, 8.86	10.59	8.90			10.28	10.58
213	11.48	9.19, 7.99	10.41	8.82, 8.77	11.82	9.09, 8.93	10.63	9.01			10.31	10.69
198	11.61	9.28, 8.01	10.43	8.92, 8.88	11.91	9.29, 9.03						
183			10.43	8.98, 8.93	11.99	9.39, 9.09						
T_c/K	295 ± 2		275 ± 2		273 ± 2							

* δ ±0.02 p.p.m. from $SiMe_4$ unless otherwise indicated.

RESULTS

Series of variable-temperature n.m.r. spectra were recorded for the ligands in [$^2H_6$]acetone and in $CDCl_3$ solutions, and for the zinc complexes in [$^2H_6$]acetone solutions only, for solubility reasons. Some of the data are reported in Tables 3—5. In $CDCl_3$ the spectra of the ligands [except, of course, acetone 4-phenyl-3-thiosemicarbazone, (V)] exhibited two resonances for the NH_2 protons, indicating hindered rotation about the C(S)–NH_2 bond, due to its partial double-bond character. For all these ligands the coalescence temperature is above 318 K. One of these two signals is almost independent of temperature suggesting its participation in intramolecular hydrogen bonding. In the case of benzaldehyde thiosemicarbazone, (II), and acetophenone thiosemicarbazone, (III),

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[6] A. V. Ablov and N. V. Gerbeleu, *Russ. J. Inorg. Chem.*, 1964, **9**, 46.

[7] M. Mathew and G. J. Palenik, *Inorg. Chim. Acta*, 1971, **5**, 349.

[8] F. J. Welcher, 'The Analytical Uses of E.D.T.A.,' Van Nostrand, New York, 1958, p. 149.

[9] A. I. Vogel, 'A Textbook of Quantitative Inorganic Analysis,' Longmans, London, 1961, p. 950.

[10] D. V. Naik and G. J. Palenik, *Acta Cryst.*, 1974, **B30**, 2396.

this signal was obscured by that of the aromatic protons; however, its shift was certainly smaller than 14—16 Hz, over the whole temperature range examined (*ca.* 90 °C), in both cases. In acetone, separation of the two NH_2 resonances was not observed for acetone thiosemicarbazone (I). The two NH_2 signals for the other compounds were closer together and both exhibited a marked downfield shift with decreasing temperature.

The rather broad NH resonance became sharper at low temperatures and exhibited a downfield shift, which indicates the absence of intramolecular hydrogen bonds. This resonance appeared at much lower field in acetone than in chloroform solution, providing evidence for hydrogen bonding to the solvent.

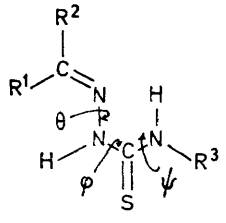
The chemical shift of both NH and NH_2 protons was dependent on concentration, suggesting the presence of intermolecular hydrogen bonding, *i.e.* the formation of dimers or polymers. In the case of compound (V) there was some difficulty in assigning the two NH resonances, since no signal was observed in the frequency region where the NH_2 resonance is generally found (see Table 3). In $CDCl_3$, however, the assignment could be safely made on the basis of the temperature shift. The lower-field resonance, which was almost independent of temperature, is assigned to the proton on N(4) (see below). In acetone solution the assignment was somewhat doubtful, since neither of the two resonances was independent of temperature. However, a marked downfield shift of the NH and NH_2 signals was observed for the other compounds of the series on going from $CHCl_3$ to acetone solutions and it may be assumed that (V) behaves in a similar way. The downfield NH signal can thus be assigned to the proton on N(4).

In some cases, at low temperature, it was possible to observe the geminal coupling of the two NH_2 protons, which behave as an AB system; the J(*gem*) values are reported in the Tables. The couplings measured in acetone compare well with the value of 2.9 Hz reported for *NN*-dimethylformamide (dmf) in the same solvent.[11]

Fewer experimental n.m.r. data were collected for the complexes (Table 5), because of their very limited solubility. In the case of dichloro(cyclohexanone thiosemicarbazone)zinc(II) [11] it was impossible to collect low-temperature data for this reason. Conductivity measurements in acetone solution indicate that the complexes dissolve essentially as neutral species. On complex formation all the resonances of the nitrogen-bonded protons shifted to low field compared with the free ligand in the same solvent. The NH_2 protons of (acetone thiosemicarbazone)-, bis(acetone thiosemicarbazone)-, and bis(benzaldehyde thiosemicarbazone)-dichlorozinc(II), (VI)—(VIII), exhibited one broad resonance at room temperature which split into two at lower temperature. The coalescence temperatures are reported in Table 5. It was not possible to calculate the rotational barrier at coalescence, since the limiting ' non-exchange ' value of the internal shift cannot be obtained from the spectra. In any case, the large number of factors affecting the resonance frequency of the *N*-bonded protons prevents a complete analysis of the spectra. A strong shielding effect was observed for all the protons of acetone thiosemicarbazone on going from complex (VI) to (VII).

DISCUSSION

X-Ray crystallographic data for several thiosemicarbazones and semicarbazones [10] show that both C(3)–N(2) and C(3)–N(4) bonds are shorter than single bonds, the latter having the larger double-bond character. Restricted rotation about these two bonds can therefore result in several different conformations, which may be obtained from the basic formula, (A), by varying the dihedral angles ϕ, θ, and ψ. Moreover, two isomers, *syn* and *anti*, can exist for each conformer depending on the relative position of the R^1 (or R^2) and NH groups. Solid-state studies, mainly *X*-ray crystal structures,[4] have shown that for several thiosemicarbazones the preferred conformation is nearly planar, with the N(2) proton *cis* to the sulphur atom. However, the deviations from planarity found experimentally do not preclude a delocalised system.



(A)

In order to compare the experimental n.m.r. results with the information obtainable from theoretical calculations of the stable conformations of our ligands, we evaluated the total energy corresponding to different conformations of compound (I) by means of the CNDO/2 method. The most significant results of the calculations are reported in Table 6. Rotation about the N(1)–N(2) bond is severely limited on steric grounds and this fact is reproduced by our results. Of interest are the theoretical results obtained by varying the dihedral angle ϕ. The two conformations (B) and (C) appear to have comparable energies and the energy barrier between them is not very high. Comparison with similar systems [12]

TABLE 6

CNDO energy values as a function of the angle ϕ for acetone thiosemicarbazone [see (A); $R^1 = R^2 = Me$ and $R^3 = H$]; $\theta = 180°$

ϕ/°	Energy*/kcal mol^{-1}
0	−50 562.62
30	−50 566.03
60	−50 561.75
90	−50 533.25
120	−50 549.75
150	−50 556.28
180	−50 566.04
210	−50.570.06
240	−50 565.13
270	−50 555.58
300	−50 550.55
330	−50 554.82

* 1 cal = 4.184 J.

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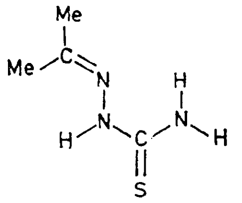
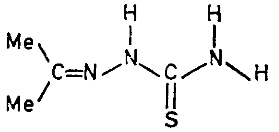
[11] B. Sunners, L. H. Piette, and W. G. Schneider, *Canad. J. Chem.*, 1960, **38**, 681.

[12] M. C. Andreocci, M. Bossa, G. Ramunni, M. Scazzocchio, D. Gattegno, and A. M. Giuliani, *J.C.S. Dalton*, 1974, 41.

suggests the presence in solution of an equilibrium between (B) and (C), fast on the n.m.r. time scale, even at low temperature.


(B)


(C)

The experimental n.m.r. results are not in disagreement with this hypothesis. However, while this conclusion may well hold in acetone solution, another more likely explanation of the experimental data can be proposed in the case of chloroform solutions. In this case, one of the NH_2 resonances is almost independent of temperature, suggesting that only conformer (B) exists in solution since it is the only one allowing formation of an intramolecular hydrogen bond between N(1) and one of the protons of the NH_2 group. This *cis* conformation, which is the same as that found in the solid state, has recently been proposed [13] for some isothiosemicarbazones. The energy contribution of this hydrogen bond, which was not taken into account in the calculations, may well stabilise (B) with respect to (C), increasing the energy barrier between them.

It follows from the above discussion, that the phenyl ring of (V), in chloroform solution, is *cis* to the thioamide sulphur. The marked deshielding of the N(4) proton of (V) as compared to the other thiosemicarbazones under study results from the almost planar structure of the C(S)–NPhH group whereby the N(4) proton lies in the deshielding region of the ring. The conformation of this group closely resembles that found in substituted thioureas [13-16] and thioamides,[17] where the bulkier substituent is generally *cis* to the thioamide sulphur, except in extremely polar solvents like D_2O.

The temperature and concentration dependences of the *N*-bonded protons may be qualitatively accounted for by the effect of several concurrent factors (hydrogen bonding to the solvent, formation of hydrogen-bonded dimers, and dipolar interactions). However, the effects of all these interactions cannot be evaluated quantitatively.

The high-field methyl resonances of (I) and (V) have been assigned to the *syn*-methyl group * on the basis of aromatic solvent-induced shifts [18] and by comparison with literature data for similar compounds.[19]

The crystal structures of benzaldehyde semicarbazone and 5-hydroxypyridine-2-carbaldehyde thiosemicarbazone [4] suggest that the preferred conformation of (II) has the NH proton *anti* to the aromatic ring. N.m.r. data on similar molecules support this hypothesis: Stenberg *et al.*,[20] who prepared both the *syn* and the *anti* isomer of benzaldehyde semicarbazone, reported a chemical shift δ 10.33 p.p.m. (relative to $SiMe_4$) for the N(2) proton of the *anti* isomer in dimethyl sulphoxide, very close to our value for (II) in acetone (δ 10.61 p.p.m.). The low-field position of this resonance compared to the other thiosemicarbazones examined by us (Table 3) is in accordance with an almost planar molecular conformation having extended electron delocalisation, as found in the solid state, and the N(2) proton lying in the plane of the ring. This point is discussed at length by Stenberg *et al.*[20] We have assigned an *anti* conformation to acetophenone thiosemicarbazone, (III), on the basis of similar arguments (crystal structure [5] and n.m.r. data [20] of closely related systems). However, since the N(2) proton does not experience the same deshielding effect as in (II), it may be inferred that it is not in the plane of the ring, *i.e.* the molecule has larger deviations from planarity and less extended electron delocalisation than does (II).

On complex formation a marked deshielding is observed for all the protons of the ligands. The most probable geometry of the 1 : 2 complexes is tetrahedral, more or less distorted, with the thiosemicarbazones acting as unidentate ligands through their sulphur atom. The chromophore is then ZnS_2Cl_2, as found for similar complexes with thioureas.[21] In the solid state, (acetone thiosemicarbazone)dichlorozinc(II), (VI), has a distorted tetrahedral geometry [7] with N(1) and S co ordinated to the metal atom together with the two halogens.

TABLE 7

CNDO energy values as a function of the angle ϕ for benzaldehyde thiosemicarbazone [see (A); R^1 = Ph and R^2 = R^3 = H]; θ = 180°

ϕ/°	Energy/kcal mol^{-1}
0	−68 097.06
60	−68 094.56
90	−68 087.14
120	−68 085.28
180	−68 099.78
240	−68 096.48
270	−68 088.26
300	−68 085.27
330	−68 090.22

Inspection of the variable-temperature n.m.r. data suggest that the N(2) proton is involved in intramolecular hydrogen bonding in (VII), bis(acetophenone thiosemicarbazone)dichlorozinc(II), (IX), and bis(acetone 4-phenyl-3-thiosemicarbazone)dichlorozinc(II), (XI). This intramolecular interaction between the co-ordinated

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* *syn* and *anti* referred to the N(2) proton.

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[14] A. S. Tompa, R. D. Barefoot, and E. Price, *J. Phys. Chem.*, 1969, **73**, 435.

[15] A. M. Giuliani, *J.C.S. Dalton*, 1972, 492.

[16] W. Walter and K. P. Ruess, *Annalen*, 1971, **743**, 167.

[17] W. Walter and K. P. Ruess, *Annalen*, 1971, **743**, 54.

[18] J. Sandstrom and B. Uppstrom, *Acta Chem. Scand.*, 1967, **21**, 2254.

[19] G. J. Martin and M. L. Martin, *Progr. N.M.R. Spectroscopy*, 1972, **8**, 5.

[20] V. I. Stenberg, P. A. Barks, D. Bays, D. D. Hammargren, and D. V. Rao, *J. Org. Chem.*, 1968, **33**, 4402.

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halogen and the NH group has been found for many similar ligands, both in the solid state [7,22,23] and in solution.[21,24] No effect of this type was observed for complex (VIII).

The formation of the 1 : 1 complexes (VI) and dichloro(cyclohexanone thiosemicarbazone)zinc(II), (X), necessarily involves a major change in the stereochemistry of the ligand, *i.e.* a change of the θ angle by *ca.* 180° to allow formation of the N(1)-Zn bond. This geometry does not allow any intramolecular hydrogen-bonding interaction, neither between N(1) and the N(4) protons nor between a co-ordinated halogen and the N(2) proton.

For all the complexes, except (IX) at low temperatures, the broad NH_2 resonance splits in two, indicating restricted rotation about the C(3)-N(4) bond, as for the free ligands. Hydrogen bonding to acetone is competitive with the intramolecular N(1) ··· H-N(4) bond, as observed for the free ligands, and the NH_2 resonances [except in the case of (VII)] have a temperature shift which may be qualitatively accounted for by hydrogen bonding to the solvent. An unexpected result is the temperature independence of one of the NH_2 resonances of (VI). This behaviour suggests an intramolecular interaction, which is forbidden by the geometry of the complex. The formation of a bimolecular adduct, stable even at *ca.* 273 K, could explain this feature. The molecular weight of the complex, at 298 K in acetone, is indeed 10—15% higher than the calculated value, supporting the hypothesis of a degree of stable molecular association even at room temperature.

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