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, NR³H·CS·NH·N:CR²R¹ (L: R¹, R² = H, Me, Ph, or $R^{1}R^{2} = C_{6}H_{11}$; $R^{3} = H$ or Ph), and their complexes [ZnCl₂L] or [ZnCl₂L₂] 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.

EXPERIMENTAL

The starting carbonyl compounds and the thiosemicarbazide were Merck reagent-grade products; 4-phenylthiosemicarbazide was a K and K reagent and ZnCl₂ an Erba RP product. Thiosemicarbazones were prepared following the procedures of Sah and Daniels.⁵ The crude

TABLE 1

Analytical data for the thiosemicarbazones

| | | Analysis (%) | | | | | | | | |
|---|--|--------------|-------|------|-------|----------|------|---|--|--|
| | | | Found | | ····· | Mr. A PC | | | | |
| Compound | Formula | С | Ň | Н | C | Ň | Н | $\mathbf{M}.\mathbf{p}. (0_{e} / \mathbf{C})$ | | |
| Acetone thiosemicarbazone, (I) | C4H9N3S | 36.5 | 32.15 | 6.95 | 36.65 | 32.05 | 6.85 | 181-183 | | |
| Benzaldehyde thiosemicarbazone, (II) | C ₈ H ₉ N ₃ S | 53.6 | 23.65 | 5.05 | 53.65 | 23.45 | 5.00 | 159-161 | | |
| Acetophenone thiosemicarbazone, (III) Cyclohexanone thiosemicarbazone. | $C_9H_{11}N_3S$ | 55.85 | 21.9 | 5.65 | 55.95 | 21.75 | 5.70 | 118-120 | | |
| (IV) Acetone 4-phenyl-3- | $\mathrm{C_7H_{13}N_3S}$ | 49.4 | 24.65 | 7.80 | 49.1 | 24.55 | 7.60 | 159-161 | | |
| thiosemicarbazone, (V) | $C_{10}H_{13}N_{3}S$ | 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 | С | N | Н | CI | M.p. $(\theta_c/^{\circ}C)$ | | |
| (Acetone thiosemicarbazone)- dichlorozinc(II), (VI) | $[ZnCl_2(C_4H_9N_3S)]$ | calc: found: | $\begin{array}{c} 24.45 \\ 24.5 \end{array}$ | $17.95 \\ 17.95$ | $15.7 \\ 15.8$ | $3.35 \\ 3.50$ | $\begin{array}{c} 26.5 \\ 25.4 \end{array}$ | 160-162 | | |
| Bis(acetone thiosemicarbazone)- dichlorozinc(II), (VII) | $[ZnCl_2(C_4H_9N_3S)_2]$ | calc: found: | $\begin{array}{c} 16.4 \\ 16.25 \end{array}$ | $\begin{array}{c} 24.1 \\ 24.15 \end{array}$ | $21.1 \\ 21.25$ | $4.50 \\ 4.65$ | $17.8 \\ 17.9$ | 240242 | | |
| Bis(benzaldehyde thiosemicarbazone)- dichlorozinc(11), (VIII) | $[\mathrm{ZnCl}_{2}(\mathrm{C}_{8}\mathrm{H}_{9}\mathrm{N}_{3}\mathrm{S})_{2}]$ | calc.: found: | $\begin{array}{c} 13.2 \\ 13.2 \end{array}$ | $\begin{array}{c} 38.85\\ 38.8 \end{array}$ | $\begin{array}{c} 17.0 \\ 16.95 \end{array}$ | $3.65 \\ 3.60$ | | | | |
| Bis(acetophenone thiosemicarbazone)- dichlorozinc(II), (IX) | $[\mathrm{ZnCl}_2(\mathrm{C_9H_{11}N_3S})_2]$ | calc.: found: | $\begin{array}{c} 12.5 \\ 12.5 \end{array}$ | $\begin{array}{r} 41.35 \\ 41.55 \end{array}$ | $\begin{array}{c} 16.1 \\ 16.3 \end{array}$ | $4.20 \\ 4.25$ | | | | |
| Dichloro(cyclohexanone thiosemicarba- zone)zinc(11), (X) | $[ZnCl_2(C_7H_{13}N_3S)]$ | calc.: found: | $\begin{array}{c} 21.25 \\ 21.6 \end{array}$ | $\begin{array}{c} 27.35 \\ 27.5 \end{array}$ | $\begin{array}{c} 13.65 \\ 13.15 \end{array}$ | $\begin{array}{r} 4.25 \\ 4.25 \end{array}$ | | 237—24 0 | | |
| Bis(acetone 4-phenyl-3-thiosemi- carbazone)dichlorozinc(II), (XI) | $[ZnCl_2(C_{10}H_{13}N_3S)_2]$ | calc.: found: | $\begin{array}{c} 11.9\\11.9\end{array}$ | $\begin{array}{c} 43.6 \\ 43.5 \end{array}$ | $\begin{array}{c} 15.25 \\ 15.05 \end{array}$ | $4.70 \\ 4.90$ | | | | |

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}.

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.

products were recrystallised several times from waterethanol 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

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 ZnCl₂ yielded two products: [ZnCl₂L], previously prepared by Ablov and Gerbeleu⁶ and characterised in the solid state by Mathew and Palenik; ' and [ZnCl₂L₂], 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[NO₃] was used to determine the chloride content.⁹ The n.m.r. spectra were recorded at 90 MHz (Bruker HX-90 spectrometer), SiMe₄ being used as internal standard and for field for the molecules investigated are from refs. 4 and 10 and were kept constant for the different conformations.

A Kholrausch SIS-Halosis FA₂-type bridge was used for the conductivity measurements.

RESULTS

Series of variable-temperature n.m.r. spectra were recorded for the ligands in [2H₆]acetone and in CDCl₃ solutions, and for the zinc complexes in [2H₆]acetone solutions only, for solubility reasons. Some of the data are reported in Tables 3-5. In CDCl₃ the spectra of the

TABLE 3

| Com- | (I) | | | | (11) | | (111) | (IV) | | | (V) | |
|-----------|--------|------------------------|-----------------|--------|------------------|--------|--------------------|--------|---------------|-----------------|--------|--------|
| T/K pound | N(2)-H | N(4) |)-H | N(2)-H | N(4)-H | N(2)-H | N(4)-H | N(2)-H | N(4) | -н | N(2)-H | N(4)-H |
| 318 | • • | | | 9.64 | b, 6.39 | 8.73 | $b, 6.29 \pm 0.06$ | 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 | $b, 6.39 \pm 0.06$ | 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 | $b, 6.49 \pm 0.03$ | 8.98 | 7.30, | 6.67 | 8.58 | 9.31 |
| 273 | 8.56 | $7.27 \pm 0.04, \circ$ | 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 | $7.30 \pm 0.04, \circ$ | 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 | $7.32 \pm 0.03, c$ | 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 <i>f</i> | 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 |

• 8 ± 0.02 p.p.m. from SiMe, unless otherwise indicated. • Obscured by aromatic protons. • Interference from CHCl₃. • Shoulder. • J(gem) 3.5 ± 0.5 Hz.

TABLE 4 Chemical shifts ^a of some thiosemicarbazones in $[{}^{2}H_{a}]$ acetone

| | | | | | | | | | | 05 | | |
|-------|-------------|-----------------|------------|--------------------|--------|------------|------------------------|---------|--|------------------------|-----------------|---------------|
| < Com | • | (I) | | (11) | | (1) | []) | | (1 | V) | | (V) |
| | nd N(2)- | H N(4)-H | N(2)-H | N(4)-H | N(2)-H | A | N(4)-H | N(2)- | шело на село на На село на село | N(4)-H | N(2)-H | N(4)-H |
| 318 | . , | | ., | | • • | | | 9.08 | ca. 7.4.0 | ca. 7.2 b | 9.04 ± 0.04 | 9.64 + 0.04 |
| 303 | 9.00 | 7.33 ± 0.08 | 10.61 | $c, 7.58 \pm 0.04$ | 9.33 | с, | $7.53 \pm 0.04 \circ$ | 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 | с, | 7.64 ± 0.06 | 9.24 | $7.53 \pm 0.04, b$ | 7.33 ± 0.05 6 | 9,23 | 9.79 |
| 273 | | /- | 10.77 | 8.04, c | 9.48 | 8.04, c ca | $1.7.76 \pm 0.03$ | 9.33 | $7.62 \pm 0.03, b$ | 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, | e | 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 * | 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 8 ± | 0.02 p. | p.m. from SiM | e4, unless | otherwise indicate | d. Dov | erlappin | g. • Obscured l | by aron | natic protons. | d J(gem) 2.2 ± 0.5 Hz. | e J(gem) 2.5 | \pm 0.5 Hz. |

TABLE 5

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

| Com- | | Q | VI) | | (VII) | | (VIII) | (I | X) | (3 | :) | () | XI) |
|------------|---|------------------------------|--|------------------|-----------------------------|------------------|----------------|--------|--------------|--------|--------|----------|----------------|
| T/K pound | 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 | 1 N(2)-F | I N(4)-H |
| 303 | 10.90 | | $, 8.28 \pm 0.06$ | 10.18 | , 8.18 | 11.38 | 8.58, | 10.33 | 8.42 | 10.9 | 8.17 | 10.03 | 10.03 |
| 288 273 | 10.98 | 8.40 ± 0 8.80 ± 0 | $0.06, 8.11 \pm 0.06$ $0.04, 7.79 \pm 0.04$ | $10.22 \\ 10.27$ | $, 8.26 \pm 0.03$, 8.36 | $11.46 \\ 11.53$ | 8.61, 8.68, | 10.40 | 8.60 | | | 10.04 | 10.13 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 |
| 243 228 | 11.30 | 9.03, 9.09, | 7.95 | 10.33 | 8.60, 8.52 | 11.68 | 8.87, 8.79 | 10.56 | 8.82 8.90 | | | 10.22 | 10.47 |
| 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 | 11.99 | 9.29, 9.03 | | | | | | |
| T_{c}/K | | 295 ± 2 | 2 | | 275 ± 2 | | 273 ± 2 | | | | | | |
| | * 8 ± 0.03 n p m from SiNe, unless otherwise indicated. | | | | | | | | | | | | |

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

* OCPE Program 141, Chemistry Department, Indiana University, Bloomington, Indiana 47401, U.S.A.

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.

ligands [except, of course, acetone 4-phenyl-3-thiosemicarbazone, (V)] exhibited two resonances for the NH, protons, indicating hindered rotation about the C(S)-NH₂ 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),

⁸ F. J. Welcher, 'The Analytical Uses of E.D.T.A.,' Van Nostrand, New York, 1958, p. 149.
A. I. Vogel, 'A Textbook of Quantitative Inorganic Analy-

sis, 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 NH₂ resonances was not observed for acetone thiosemicarbazone (I). The two NH₂ 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 NH2 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 NH₂ resonance is generally found (see Table 3). In CDCl₃, 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 NH₂ signals was observed for the other compounds of the series on going from CHCl₃ 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 lowtemperature 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 NH2 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).

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

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 R¹ (or R²) 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.

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)

TABLE 6

 $\begin{array}{ll} \mbox{CNDO energy values as a function of the angle ϕ for acetone this emicarbazone [see (A); $R^1 = R^2 = Me$ and $R^3 = H]; $\theta = 180^\circ$ \end{array}$

| ¢ /° | Energy*/kcal mol ⁻¹ |
|-------------|--------------------------------|
| 0 | $-50\ 562.62$ |
| 30 | -50566.03 |
| 60 | $-50\ 561.75$ |
| 90 | $-50\ 533.25$ |
| 120 | -50549.75 |
| 150 | -50556.28 |
| 180 | $-50\ 566.04$ |
| 210 | -50.570.06 |
| 240 | -50 565.13 |
| 270 | - 50 555.58 |
| 300 | -50550.55 |
| 330 | $-50\ 554.82$ |
| * 1 | cal = 4.184 J. |

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 systems¹²

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.



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 NH₂ 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 NH₂ 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 thioureas¹³⁻¹⁶ 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

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

- A. M. Giuliani, J.C.S. Dalton, 1972, 492.
 W. Walter and K. P. Ruess, Annalen, 1971, 743, 167.
 W. Walter and K. P. Ruess, Annalen, 1971, 743, 54.

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

The crystal structures of benzaldehyde semicarbazone and 5-hydroxypyridine-2-carbaldehyde thiosemicarbazone⁴ 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 SiMe₄) 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. data²⁰ 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 ZnS₂Cl₂, 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 $R^2 = R^3 = H_1$; $\theta = 180^{\circ}$

| ø /° | Energy/kcal mol ⁻¹ |
|-------------|-------------------------------|
| 0 | -68097.06 |
| 60 | $-68\ 094.56$ |
| 90 | $-68\ 087.14$ |
| 120 | $-68\ 085.28$ |
| 180 | -68 099.78 |
| 240 | -68096.48 |
| 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

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

¹³ C. Yamazaki, Canad. J. Chem., 1975, 53, 610.

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, 1968, **93**, 4402. 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 hydrogenbonding 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) \cdots H-N(4) bond, as observed for the free ligands, and the NH_2 resonances [except in the case of (VII)] have a tem-

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perature shift which may be qualitatively accounted for by hydrogen bonding to the solvent. An unexpected result is the temperature independence of one of the NH₂ 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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