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Metal Complexes of Symmetric and Non-symmetric Tetradentate Schiff Bases derived from 1-(2-mercaptophenyl)-ethanone

RICHARD C. COOMBES, JEAN-PIERRE COSTES† and DAVID E. FENTON*

Department of Chemistry, The University, Sheffield, S3 7HF, U.K.

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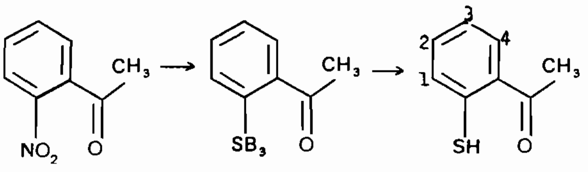
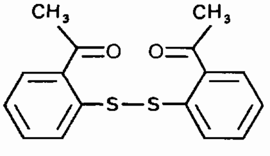
Recent interest in the chemistry of thiosalicylidineimines [1] prompts us to report some of our work concerning metal complexes of symmetric and non-symmetric Schiff bases derived from 1-(2-mercaptophenyl)-ethanone, (H_2–mpe). This precursor [2] is prepared from 2-nitroacetophenone via conversion first to (2-benzylthio)acetophenone using benzyl mercaptan and lithium hydroxide in methanol according to the technique of Meth-Cohn and Tarnowski [3], and subsequent removal of the protecting group with aluminium trichloride in benzene [4] (Scheme).



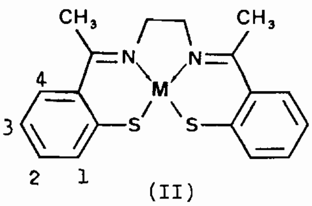
(H_2-mpe)

The reaction of H_2-mpe with nickel(II) ethanoate in degassed ethanol and under dinitrogen gave maroon needles of the compound $Ni(mpe)_2$. $C_{16}H_{14}O_2S_2Ni$ requires C = 53.19, H = 3.68, S = 17.73%; *found,* C = 53.22, H = 3.56, S = 17.76%: i.r. 1660 cm^{-1} ($\nu_{C=O}$). A similar reaction with copper(II) ethanoate led to the isolation of white crystals of (I). This structure was assigned on the basis of i.r. (1660 cm^{-1}, ($\nu_{C=O}$), no ν_{SH}); m.s. (M = 302, P^+ at m/e = 302) and microanalytical data ($C_{16}H_{14}O_2S_2$ requires C = 63.58, H = 4.64, S = 21.19%; *found,* C = 63.08, H = 4.09, S = 20.59%). It is suggested that the oxidation of H_2mpe would be accompanied by the reduction of copper(II) to copper(I) as has been suggested previously for the reactions of related β-mercaptoketones with copper(II) salts [5]. An earlier study of the complexing properties of H_2–mpe gave no isolable complexes [6]. We have found that it is essential to work in a dinitrogen atmosphere in order to facilitate product isolation.



(I)

Symmetrical copper(II) and nickel(II) Schiff base complexes were prepared by template procedures using degassed solvents and under a dinitrogen atmosphere. Early attempts to prepare such complexes in the atmosphere from preformed Schiff bases were unsuccessful—this was because the Schiff base was found to be present as the cyclic diimine disulphide as it too had been prepared on the open bench.



(II)

H_2–mpe and the metal(II) ethanoate were refluxed together for 15 minutes in 2:1 stoichiometric ratio in ethanol and then 1,2-diaminoethane was added in correct molar proportion to the solution prior to refluxing for several hours. The metal complexes (II, M = Cu, Ni) were isolated on cooling as red-brown (Cu) and light brown (Ni) powders. $C_{18}H_{18}N_2S_2Cu$ requires C = 55.45, H = 4.62, N = 7.19, S = 16.43%; *found,* C = 55.57, H = 4.64, N = 7.03, S = 16.38%. I.r. 1580 cm^{-1} ($\nu_{C=N}$): $C_{18}H_{18}N_2S_2Ni$, H_2O requires C 53.60, H = 4.96, N = 6.95, S = 15.88%; *found,* C = 53.86, H = 4.64, N = 6.69, S = 16.62%. I.r. 1590 cm^{-1} ($\nu_{C=N}$). The complexes, by comparison with the corresponding phenolic species [7], are likely to be square planar. The ^1H nmr spectrum of the nickel complex was complicated and suggested that a possible hydrolysis was occurring. A sample of (II, M = Ni) was prepared from the reaction of $Ni(mpe)_2$ with 1,2-diaminoethane in ethanol in the presence of $CH_3C(OCH_3)CH_3$ and under an argon atmosphere. The ^1H nmr in $CDCl_3$ gave the following signals (δ = 2.47 (6H, s, CH_3), 3.74 (4H, s, CH_2), 7.02 (2H, t, $H_{2/3}$), 7.04 (2H, t, $H_{3/2}$), 7.51(2H, d, H_1), and 7.76 (2H, d, H_4) ppm). The ^1H nmr of $Ni(mpe)_2$ was also run in $CDCl_3$ and gave the following sharp signals suggesting that this species is also square planar (δ = 2.59 (6H, s, CH_3), 6.98 (2H, t, H_3), 7.15 (2H, t, H_2), 7.64 (2H, d, H_1) and 7.79 (2H, d, H_4) ppm).

The reaction of H_2–mpe with the tridentate 'half-unit' Schiff base prepared from 2,4-pentanedione and 1,2-diaminoethane [8] gave the non-symmetric

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*Author to whom correspondence should be addressed.

†Present address: Laboratoire de Chimie de Coordination du C.N.R.S., 205 route de Narbonne, 31400 Toulouse, France.

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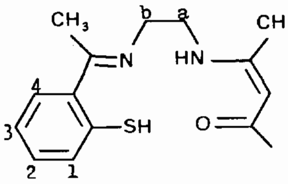
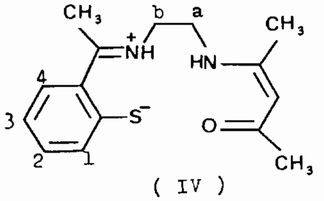


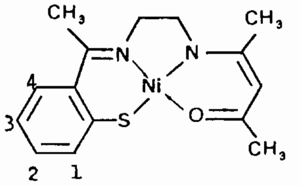
(III)

Schiff base (III). This orange compound was characterised by microanalysis ($C_{15}H_{20}N_2OS$ requires C = 65.22, H = 7.25, N = 10.14, S = 11.59%; *found,* C = 65.09, H = 7.21, N = 9.92, S = 10.22%), m.s. (M = 276, P^+ at m/e = 276), i.r. (2350 (bd, ν_{NH^+}), 1630 (sh, $\nu_{C=N}$), 1605 ($\nu_{C=O}$) and 1590 ($\nu_{C=N}$) cm^{-1} and ^1H nmr spectra ($CDCl_3$: δ = 1.94 (3H, s, CH_3–CNH), 1.99 (3H, s, CH_3–C=O), 2.55 (3H, s, CH_3–C=N), 3.78 (2H, q, CH_2^a), 3.90 (2H, t, CH_2^b), 4.99 (1H, s, CH), 6.88 (1H, t, H_3), 7.14 (1H, t, H_2), 7.62 (1H, d, H_1), 7.73 (1H, d, H_4) and 10.89 (1H, s, NH) ppm). The compound (III) is soluble in organic solvents and is better formulated as the zwitterion (IV). There is no –SH signal in the nmr, or i.r, spectra and integration shows that there is only one NH proton at 10.89 ppm not two as expected for (III). There is a broad band in the i.r at 2350 cm^{-1} assignable to the $=\overset{+}{N}H$ and a shoulder at 1630 cm^{-1} for the $\nu_{C=N}$ of the Schiff base in good agreement with a movement to higher frequency on zwitterion formation. Such zwitterionic imminium structures have been presented for similar Schiff bases derived from 2-mercaptobenzaldehyde [9].



(IV)

Nickel (II) ethanoate reacted with (III) in ethanol under dinitrogen to give light green crystals of (V). This complex was characterised by microanalysis ($C_{15}H_{18}N_2OSNi$ requires C = 54.10, H = 5.41, N = 8.42, S = 9.62%; *found*, C = 53.98, H = 5.67, N = 8.10, S = 9.48%), m.s. (M = 332, P^+ at m/e = 332), i.r. (1585 with shoulders at 1580, 1570 and 1560 cm^{-1} ($\nu_{C=N} + \nu_{C=O} + \nu_{C=C}$)) and ^1H nmr spectra ($CDCl_3$: δ = 1.81 (3H, s, CH_3–CNH), 1.91 (3H, s, CH_3–C=O), 2.50 (3H, s, CH_3–C=N), 3.13 (2H, m, CH_2), 3.74 (2H, m, CH_2), 4.90 (1H, s, CH), 6.90 (1H, t, $H_{3/2}$), 7.05 (1H, t, $H_{2/3}$), 7.36 (1H, d, $H_{4/1}$) and 7.72 (1H, d, $H_{1/4}$) ppm). The complex is assigned a square planar geometry by analogy with the determined structures of the related copper(II) and nickel(II) complexes of the non-symmetric Schiff base derived from pyrrole-2-carbaldehyde and the acac-en 'half-unit' [10], and as indicated by the availability of the nmr spectrum.



(V)

The reaction of (III) with copper(II), cobalt(II) and zinc(II) ethanoates also gave complexes. However for these complexes it has not yet been possible to obtain clearly defined microanalytical data. The m.s. show that the 1:1 complexes have been formed as parent ions are found at the required mass numbers for the molecular weights.

Acknowledgments

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References

1 P. J. Marini, K. S. Murray and B. O. West, *J. Chem. Soc. Dalton Trans.*, 143 (1983), and references therein.
2 R. C. Coombes and D. E. Fenton, *Phosphorus and Sulphur., 14,* 139 (1983).
3 O. Meth-Cohn and B. Tarnowski, *Synthesis,* 56 (1978).
4 K. Clarke, C. G. Hughes and R. M. Scrowston, *J. Chem. Soc. Perkin I.*, 356 (1973).
5 H. Tanaka and A. Yokoyama, *Chem. Pharm. Bull. (Japan), 8,* 1012 (1960).
6 H. Tanaka and A. Yokoyama, *Chem Pharm. Bull. (Japan), 10,* 25 (1962).
7 T. S. Cannan and A. Chakravorty, *Inorg. Chem., 9,* 1153 (1970).
8 J-P. Costes and G. Cros, *Comptes Rendus. Séances Acad. Sci. Ser. 2., 294,* 173 (1982).
9 M. F. Corrigan, I. D. Rae and B. O. West, *Austral. J. Chem., 31,* 587 (1978).
10 H. Adams, N. A. Bailey, J-P. Costes, D. E. Fenton and J. R. Tate, unpublished data and Poster A25, *International Conference on Inorganic Stereochemistry,* Reading, England, 1982.