Inorganica Chimica Acta, 29 (1978) L241–L242
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The Characterization of N,N^1-Ethylenebis(thiophen-2-carbaldimine)

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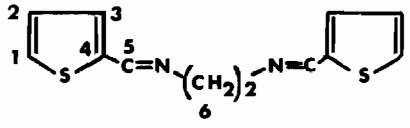
Received May 18, 1978

Schiff-base ligands continue to find wide application in coordination chemistry, but the nitrogen/oxygen donor groups are, more and more, being superseded by ligands containing other donors, especially sulphur.

The ligand N,N^1-ethylenebis(thiophen-2-carbaldimine) is a very attractive ligand in many ways, though few studies [1, 2] have been performed with it. As well as the imine linkages resulting from the Schiff-base condensation reaction,



this ligand also contains heterocyclic sulphur donors. We are currently investigating the general donor properties of this chelate and wish here to report a much improved preparation in high yield. We have also been able to thoroughly characterise the compound by nuclear magnetic resonance and mass spectroscopy.

TABLE I. C-13 Chemical Shifts for Ligand.[a]

Carbon	δ, ppm	Coupling Constants, Hz
1	127.33	$^1J_{CH} = 170$
2	130.45	$^1J_{CH} = 180$
3	128.79	$^1J_{CH} = 180$
4	142.45	
5	155.95	$^1J_{CH} = 160.1, {}^3J_{CH} = 11.6$
6	61.02	$^1J_{CH} = 138.8, {}^3J_{CH} = 11.6$

[a] Relative to TMS (downfield).

TABLE II. Mass Spectrum of Ligand.[a]

m/e	Relative Intensity	Ion
248	1.1	$C_{12}H_{12}N_2S_2$
139	84.7	C_7H_9NS
137	34.3	C_7H_7NS
124	57.0	C_6H_6NS
111	42.8	C_5H_5NS
110	48.6	C_5H_4NS
97	100.0	C_5H_5S
45	15.7	CHS
39	10.7	C_3H_3

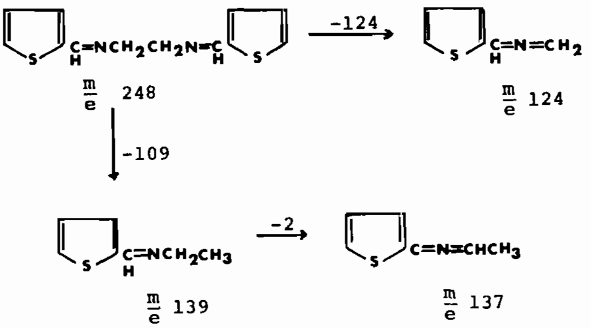
[a] Peaks below m/e 35 were not considered. Relative intensities less than 10 were not included.

Experimental

Freshly distilled ethylenediamine (13 cm^3) in absolute ethanol (30 cm^3) was slowly added to a hot stirred solution of thiophene-2-carbaldehyde (15 cm^3) in absolute ethanol (30 cm^3). The mixture was gently refluxed for *ca.* 2 hr and then the volume of the solution was reduced to 30 cm^3 by rotatory evaporation. The mixture was allowed to cool at room temperature overnight and this produced copious white crystals. Recrystallization was affected from hot absolute ethanol. The resulting crystalline material was dried *in vacuo* over P_2O_5 for one day. M.Pt. 88.5 °C. Yield 88%. *Anal.*: Calculated for $C_{12}H_{12}N_2S_2$, C, 58.0; H, 4.9; N, 11.3; S, 25.8%. Found, C, 57.0; H, 4.9; N, 11.3; S, 25.0%.

Discussion

The ligand has been prepared by a facile route in almost quantitative yield. The infrared spectrum shows no evidence for N–H bonds, and ν(C=N) appears at 1630 cm^{-1}. The ^{1}H n.m.r. spectrum exhibits methylene (singlet, δ3.95), aromatic (multiplet centered at δ7.2) and imine (singlet, δ8.38)



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signals in the ratio 4:6:2, as expected. The ^{13}C n.m.r. spectral data are listed in Table I, assignments being made by analogy with similar systems [3]. The mass spectrum is reported in Table II and the fragmentation paths are shown in the Scheme.

Rearrangement upon electron bombardment or by reaction with H^+ upon ionisation is observed.

References

1 G. L. Eichorn and J. C. Bailar, *J. Am. Chem. Soc., 75,* 2905 (1953).
2 A. C. Braithwaite, C. E. F. Richard and T. N. Waters, *J. Chem. Soc. Dalton,* 2149 (1975).
3 G. C. Levy and G. L. Nelson, "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists", Wiley–Interscience, New York, 1972.