

Synthesis of Low Spin $[\text{Mn}^{\text{II}}(\text{L}^2)_2]\text{I}_2 \cdot 2\text{MeOH}$ and $[\text{Cu}^{\text{III}}(\text{L}^1)]$ via Condensation of *S*-Methylisothiosemicarbazide and Pentane-2,4-dione in the Presence of Air†

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The complexes $[\text{Mn}^{\text{II}}(\text{L}^2)_2]\text{I}_2 \cdot 2\text{MeOH}$ **1** and $[\text{Cu}^{\text{III}}(\text{L}^1)]$ **2** have been synthesized by a template-like reaction between *S*-methylisothiosemicarbazide and pentane-2,4-dione, with MnCl_2 and $\text{Cu}_2(\text{MeCO}_2)_4 \cdot 2\text{H}_2\text{O}$, respectively, in MeOH by air oxidation; both species have been characterized by X-ray crystallography.

The fascinating work of Gerbeleu *et al.*¹ and Leovac *et al.*¹ has convincingly shown that the trianionic ligand L^1 (Scheme 1)† forms surprisingly stable complexes of iron in the rather unusual oxidation state +iv. With nickel(II) on the other hand the ligand generates in its diprotonated monoanionic form a square planar diamagnetic nickel(II) complex² (Scheme 1). The ligand L^1 is prepared *in situ* by a condensation reaction of *S*-methylisothiosemicarbazide hydroiodide and pentane-2,4-dione in refluxing ethanol or methanol in the presence of air.^{2‡}

† $\text{L}^1 =$ dimethyl 2,2'-(1,3-dimethylpropane-1,3-diylidene)bishydrazinecarboximidothioate (3⁻) [or¹ pentane-2,4-dione bis-(*S*-methylisothiosemicarbazionate (3⁻)); $\text{L}^2 =$ methyl-4,5-dihydro-5-([imino(methylthio)methyl]azo)-3,5-dimethyl-1*H*-pyrazole-1-carboximidothioate.

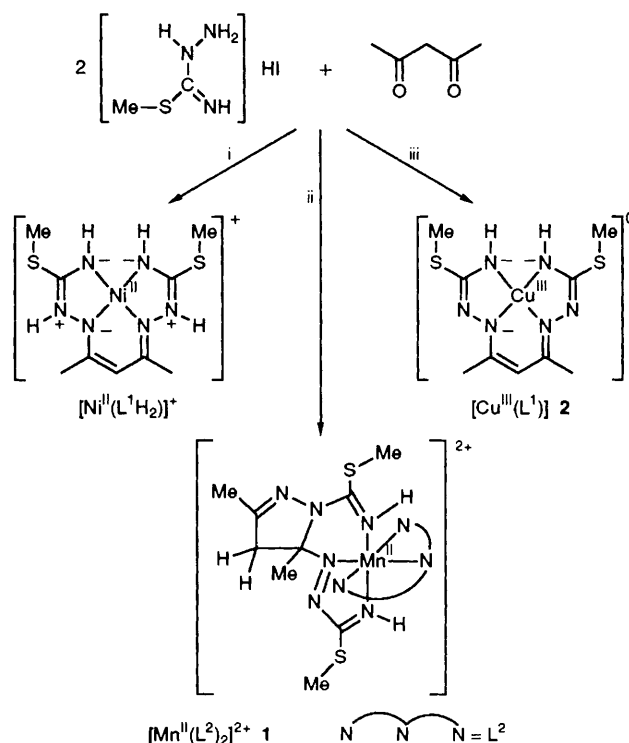
‡ *General synthetic procedures.* The ligands were prepared *in situ* as follows. 6.4 mmol (1.50 g) *S*-methylisothiosemicarbazide hydroiodide³ (6.4 mmol, 1.50 g), Na_2CO_3 (7.5 mmol, 0.80 g) and pentane-2,4-dione (3.2 mmol, 0.32 g) were suspended in absolute methanol (40 ml) and heated at reflux for 20 min in the presence of air.

$[\text{Mn}^{\text{II}}(\text{L}^2)_2]\text{I}_2 \cdot 2\text{MeOH}$ **1**: the above cooled and filtered, slightly yellow solution was purged with argon and MnCl_2 (1.6 mmol, 0.20 g), added. The colourless solution was stirred under argon for 60 min, after which time the solution was cooled to 0 °C and stirred for 2 h in the presence of air. A colour change to deep green was observed. After storage of the solution at -20 °C for 2 days green-black needles of **1** had formed in 28% yield. UV-VIS (MeCN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$): 246 (3.4×10^4), 362 (3.5×10^3), 458 (3.0×10^3), 486sh (2.4×10^3) and 668 (2.6×10^3).

$[\text{Cu}^{\text{III}}(\text{L}^1)]$ **2**: to the above ligand solution was added under argon $\text{Cu}_2(\text{MeCO}_2)_4 \cdot 2\text{H}_2\text{O}$ (1.6 mmol, 0.64 g). After stirring for 1 h at ambient temperature air was bubbled through the solution for 30 min which resulted in the formation of a green solution. At -20 °C green-black crystals of **2** formed within 24 h in 18% yield. 80 MHz ¹H NMR(CDCl_3) δ 7.05 (s, 1H, =C-H), 5.35 (s, 2H, NH), 2.75 (s, 6H, Me) and 2.60 (s, 6H, Me); UV-VIS (MeCN) $\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{l mol}^{-1} \text{cm}^{-1}$): 725 (3.4×10^3), 376 (1.43×10^4), 315 (3.22×10^{-4}) and 247 (2.22×10^4).

Both **1** and **2** gave satisfactory elemental analyses (C, H, N, S, metal).

We have discovered that a second ligand L^2 is formed in *ca.* 28% yield in this reaction mixture in the presence of manganese(II) and oxygen. L^2 may be regarded as an oxidation product of $(\text{L}^1)^{3-}$. The neutral molecule L^2 † forms the stable green-black low spin manganese(II) (t_{2g}^5) complex



Scheme 1 Synthetic routes: i, ref. 3(b); ii, MeOH, MnCl_2 , O_2 ; iii, $\text{Cu}_2(\text{MeCO}_2)_4 \cdot 2\text{H}_2\text{O}$, MeOH, O_2

[Mn(L²)₂]₂·2MeOH **1** which was characterized by elemental analysis, temperature-dependent susceptibility measurements, ESR spectroscopy and X-ray crystallography.

Fig. 1 shows the structure of the dication [Mn(L²)₂]²⁺ in crystals of **1**.[§] Two tridentate ligands L² are coordinated meridionally (N₆ donor set). The polyhedron around the metal ion is best described as a Jahn–Teller compressed octahedron with two short Mn–N distances at 1.89(1) Å in *trans* positions with respect to each other and four longer equatorial Mn–N bonds (av. 1.985 Å). On the other hand, the observed compression may also be due to the restricted bite of the tridentate chelate L². The average Mn–N distance in **1** is

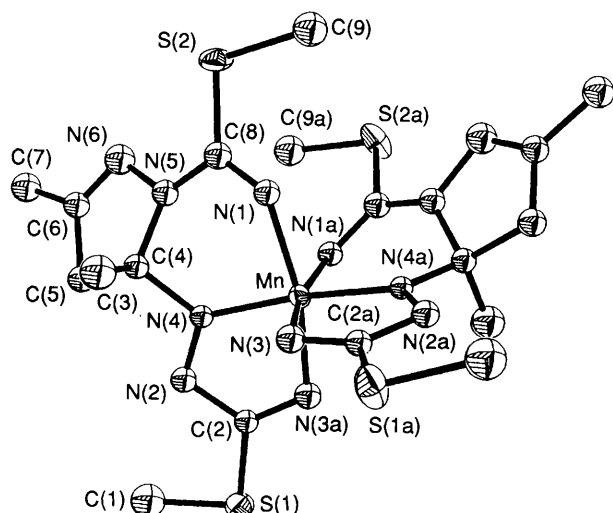


Fig. 1 Structure of the dication in crystals of [Mn(L²)₂]₂·2MeOH. Selected bond distances (Å) and angles (°): Mn–N(1) 2.02(1); Mn–N(3) 1.95(1); Mn–N(4) 1.89(1); S(1)–C(1) 1.82(2); S(1)–C(2) 1.75(2); S(2)–C(8) 1.75(1); S(2)–C(9) 1.84(2); N(1)–C(8) 1.29(2); N(2)–N(4) 1.30(2); N(2)–C(2) 1.38(1); N(3a)–C(2) 1.30(2); N(4)–C(4) 1.49(1); N(5)–N(6) 1.44(2); N(5)–C(8) 1.34(2); N(6)–C(6) 1.27(2); C(3)–C(4) 1.56(2); N(5)–C(4) 1.48(2); C(4)–C(5) 1.57(2); C(5)–C(6) 1.54(2); C(6)–C(7) 1.53(2); N(1)–Mn–N(3) 92.6(4); N(1)–Mn–N(4) 90.5(4); N(1)–Mn–N(1a) 88.7(6); N(1)–Mn–N(3a) 168.0(4); N(1)–Mn–N(4a) 95.0(4); N(3)–Mn–N(4) 97.0(4); N(3)–Mn–N(4a) 77.5(4); N(4)–Mn–N(4a) 172.4(5).

[§] *Crystal data*: **1**: C₂₀H₄₀I₂MnN₁₂O₂S₄, orthorhombic, space group *Fdd*, *a* = 18.406(4), *b* = 28.793(6), *c* = 29.076(6) Å, *V* = 15409(8) Å³, *Z* = 16, *D_c* = 1.582 g cm⁻³. A Siemens P4 diffractometer, Mo-K α radiation (graphite monochromator), was used at 173 K (slow decomposition of the crystal in the X-ray beam was observed). Intensities are corrected for this decay). 2546 reflections were collected, of which 1599 unique data with *F* \geq 4.0 σ (*F*) were used in refinement. The structure was solved by direct methods; the hydrogen atoms were not included in the refinement: anisotropic thermal parameters were used for I, Mn, S atoms only. Least-squares full-matrix refinement converged to final agreement factors of *R* = 0.067 and *R_w* = 0.070 for 111 variables. The solvent MeOH molecule is severely disordered.

For **2**: C₉H₁₅CuN₆S₂, triclinic space group *P* $\bar{1}$, *a* = 9.668(2), *b* = 10.769(2), *c* = 14.918(2) Å, α = 70.87(1), β = 77.38(1), γ = 73.01(2)°, *V* = 1390.4(4) Å³, *Z* = 4. *D_c* = 1.60 g cm⁻³. The same diffractometer was used as above at 293 K (Mo-K α radiation). 8490 reflections were collected, of which 5422 unique data with *F* \geq 4.0 σ (*F*) were used in the refinement. The structure was solved by direct methods; all the hydrogen atoms were located and included in the refinement. *R* = 0.035; *R_w* = 0.034.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

ca. 0.29 Å shorter than in high-spin manganese(II) complexes {e.g. 2.279(6) Å in⁴ [Mn(NH₃)₆]²⁺}. Each ligand L² is bound *via* two imine nitrogen atoms and one diimine type nitrogen [N(4)]. The distance N(2)–N(4) at 1.30 Å is short which indicates considerable double bond character. The five-membered dihydropyrazole ring is not bound to the metal ion. The distance N(5)–N(6) at 1.44 Å clearly indicates an N–N single bond whereas the distance N(6)–C(6) at 1.27(2) Å represents a C=N double bond.

From temperature-dependent magnetic susceptibility measurements (80–298 K) slightly temperature-dependent magnetic moments of 2.02 μ_B at 80 K and 2.12 μ_B at 298 K have been calculated which agree well with other low spin manganese(II) complexes with an *S* = 1/2 ground state.⁵ The X-band ESR spectrum of a frozen acetonitrile solution of **1** at 10 K exhibits a signal at *g* = 2.03 which shows hyperfine structure (*ca.* 6 lines) confirming the *S* = 1/2 ground state of **1**.

When to the same reaction mixture of the *in situ* generated ligand was added Cu₂^{II}(MeCO₂)₄·2H₂O at ambient temperature and air was passed through the solution, green-black microcrystals of [Cu^{III}(L¹)] **2** were obtained in 18% yield. Elemental analysis, FAB mass spectrometry (molecular ion peak, *m/z* = 334) and the observed diamagnetism (¹H NMR) corroborate the formulation as stable copper(III) complex [Cu^{III}(L¹)] **2**. Fig. 2 shows the structure of a hydrogen bonded pair of neutral molecules in crystals of **2** [N(1)–H \cdots N(11) 3.100(4) Å]. In agreement with this hydrogen bonding scheme two N–H stretching modes are observed in the IR spectrum (KBr disc): a sharp band at 3363 cm⁻¹ which is assigned to the N–H group not involved in hydrogen bonding and a broader band at 3215 cm⁻¹ of the N–H \cdots N group. The geometry around the Cu^{III} ion (d⁸) is intermediate between square planar and tetrahedral; the Cu–N distances are short (av. 1.898 Å) which is in agreement with a few other crystallographically characterized⁶ square planar Cu^{III} complexes with a CuN₄ core. The axial positions at the Cu ions are unoccupied.

In conclusion, this work reinforces the notion that *S*-alkylated isothiocarbazide derived ligands when coordinated to

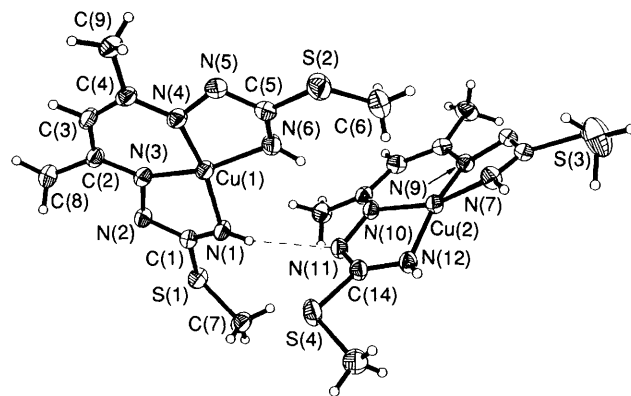


Fig. 2 Structure of the two crystallographically independent neutral molecules [Cu^{III}(L¹)] in crystals of **2**. Small open circles represent crystallographically located and refined hydrogen atoms. Selected bond distances (Å) and angles (°) for one neutral molecule: Cu(1)–N(1) 1.885(3); Cu(1)–N(3) 1.907(2); Cu(1)–N(4) 1.902(2); Cu(1)–N(6) 1.899(2); S(1)–C(1) 1.765(3); S(1)–C(7) 1.799(5); S(2)–C(5) 1.756(3); S(2)–C(6) 1.782(5); N(1)–C(1) 1.321(3); N(2)–N(3) 1.379(3); N(2)–C(1) 1.336(4); N(3)–C(2) 1.350(4); N(4)–N(5) 1.374(3); N(4)–C(4) 1.346(4); N(5)–C(5) 1.338(4); N(6)–C(5) 1.317(4); C(2)–C(3) 1.396(4); C(2)–C(8) 1.495(4); C(3)–C(4) 1.389(4); C(4)–C(9) 1.504(5); N(1)–Cu(1)–N(3) 82.6(1); N(1)–Cu(1)–N(4) 164.9(1); N(3)–Cu(1)–N(4) 95.9(1); N(1)–Cu(1)–N(6) 103.9(1); N(3)–Cu(1)–N(6) 161.5(1); N(4)–Cu(1)–N(6) 82.2(1); N(1)–H(1N) 0.757(30).

metal ions exert a very strong ligand field and are capable of stabilizing high oxidation states.

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