Electronic Supplementary Information for Dalton Transactions


# Supporting Information

# Ferromagnetic coupled μ-phenoxo-μ-carboxylato heterodinuclear complexes based on the Cr(salen) moiety: structural and magnetic characterization.

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**Crystallographic characterization of complex 1.**

Complex **1** is the first direct structural evidence of the identity of this molecule as up to now there were only two reported examples of structurally characterized compounds, both of them with this moiety as a bridging unit towards different metallic fragments.[1]

X-ray measurements of single crystals of **1** revealed the *trans* configuration of this dicyano anion with a NC-Cr-CN, C(48)-Cr(1)-C(46), angle of 175.5(4) °. The Cr(III) ion is placed in an axially elongated octahedron (Figure S1) with longer Cr-CN distances, Cr(1)-C(46), 2.112(9) Å and Cr(1)-C(48), 2.144(9) Å and shorter Cr-O, Cr-N equatorial distances in the *salen* ligand plane, Cr(1)-O(1), 1.936(5) Å, Cr(1)-O(2) , 1.938(6) Å and Cr(1)-N(1), 2.012(7), Å Cr(1)-N(3), 1.996(7) Å. The observed equatorial distances are in good agreement with the observed in other structurally characterized *trans*-Cr(salen) complexes, for examples see Ref. 2. On the other hand Cr-CN distances are larger than the observed ones in the other cationic dicyano complexes but similar to the observed ones in the cyano bridged complex $[Cr(salen)(CN)_2]_2[Mn(phen)_2]$.[3] Cyanide C-N distances are in the usual range for Cr cyanide complexes with N(2)-C(46), 1.162(9) Å and N(4)-C(48), 1.138(9) Å.[4] The $PPh_4^+$ cation is to some extent π-stacked with the *salen* ring with a mean ring to ring distance of *ca.* 4 Å. The water solvent molecule is hydrogen bonding the nitrogen cyanide atoms as usually observed in cyano complexes crystal structures (see Figure S2). For selected distances and angles see Table S1.

(1) a) Ni, Z. H.; Zhang, L. F.; Ge, C. H.; Cui, A. L.; Kou, H. Z.; Jiang, J. Z. *Inorg. Chem. Commun.* **2008,** *11,* 94-96. b) Li, H.; Zhong, Z. J.; You, X. Z.; Chen, W. *J. Coord. Chem.* **1997,** *42,* 271-281.

(2) (a) Darensbourg, D. J.; Mackiewicz, R. M. *J. Am. Chem. Soc.* **2005,** *127,* 14026-14038; (b) Li, H.; Zhong, Z. J.; You, X. Z.; Chen, W. *Polyhedron*. **1997,** *16,* 1119-1122; (c) Coggon, P.; McPhail, A. T.; Mabbs, F. E.; Richards, A.; Thornley, A. S. *J. Chem. Soc. A-Inorg. Phys. Theor.* **1970,** 3296-3303.

(3) Ni, Z. H.; Zhang, L. F.; Ge, C. H.; Cui, A. L.; Kou, H. Z.; Jiang, J. Z. *Inorg. Chem. Commun.* **2008,** *11,* 94-96.

4) (a) Lessard, R. B.; Heeg, M. J.; Buranda, T.; Perkovic, M. W.; Schwarz, C. L.; Yang, R. D.; Endicott, J. F. *Inorg. Chem.* **1992,** *31,* 3091-3103; (b) Hemmings, A. M.; Lisgarten, J. N.; Palmer, R. A.; Gazi, D. M. *Acta Crystallogr. Sect. C-Cryst. Struct. Commun.* **1990,** *46,* 205-207; (c) Albores, P.; Slep, L. D.; Weyhermuller, T.; Rentschler, E.; Baraldo, L. M. *Dalton Trans.* **2006,** 948-954; (d) Yang, J. Y.; Shores, M. P.; Sokol, J. J.; Long, J. R. *Inorg. Chem.* **2003,** *42,* 1403-1419; (e) Toma, L.; Lescouezec, R.; Vaissermann, J.; Delgado, F. S.; Ruiz-Perez, C.; Carrasco, R.; Cano, J.; Lloret, F.; Julve, M. *Chem.-Eur.J.* **2004,** *10,* 6130-6145.

**Table S1**. Selected Bond Lengths (Å) and Bond Angles (deg) of Compound **1**.

| | **1** |
|---|---|
| Cr(1) – O(1) | 1.936(5) |
| Cr(1) – O(2) | 1.938(6) |
| Cr(1) – N(3) | 1.996(7) |
| Cr(1) – N(1) | 2.012(7) |
| Cr(1) – C(46) | 2.112(9) |
| Cr(1) – C(48) | 2.144(9) |
| N(4) – C(48) | 1.138(9) |
| N(2) – C(46) | 1.162(9) |
| C(46) – Cr(1) – C(48) | 175.5(4) |

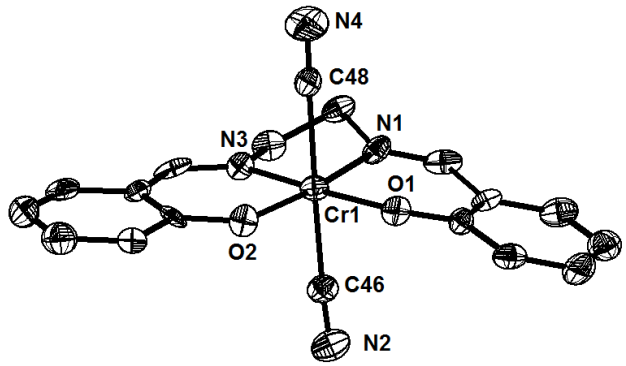


**Figure S1**. *ORTEP* representation of complex **1**. Ellipsoid probability: 50%. Hydrogen atoms have been omitted for clarity.

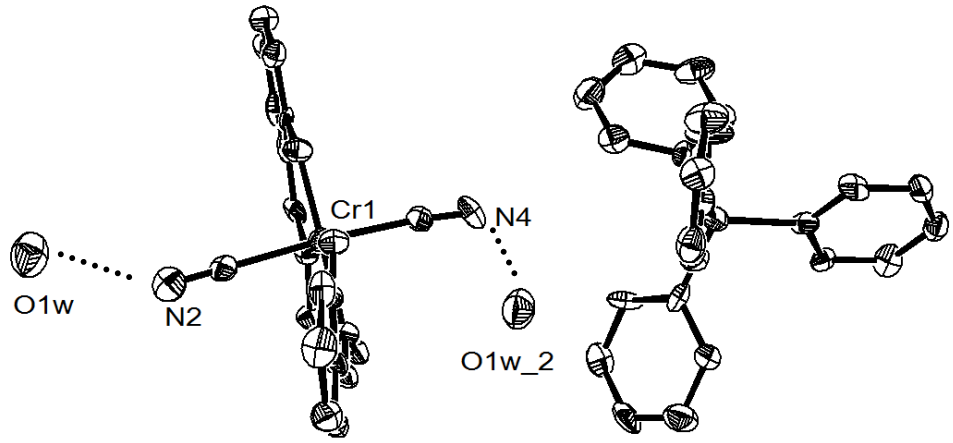


**Figure S2**. *ORTEP* representation of complex **1** showing water – cyanide H-interactions. Ellipsoid probability: 50%. Hydrogen atoms have been omitted for clarity.

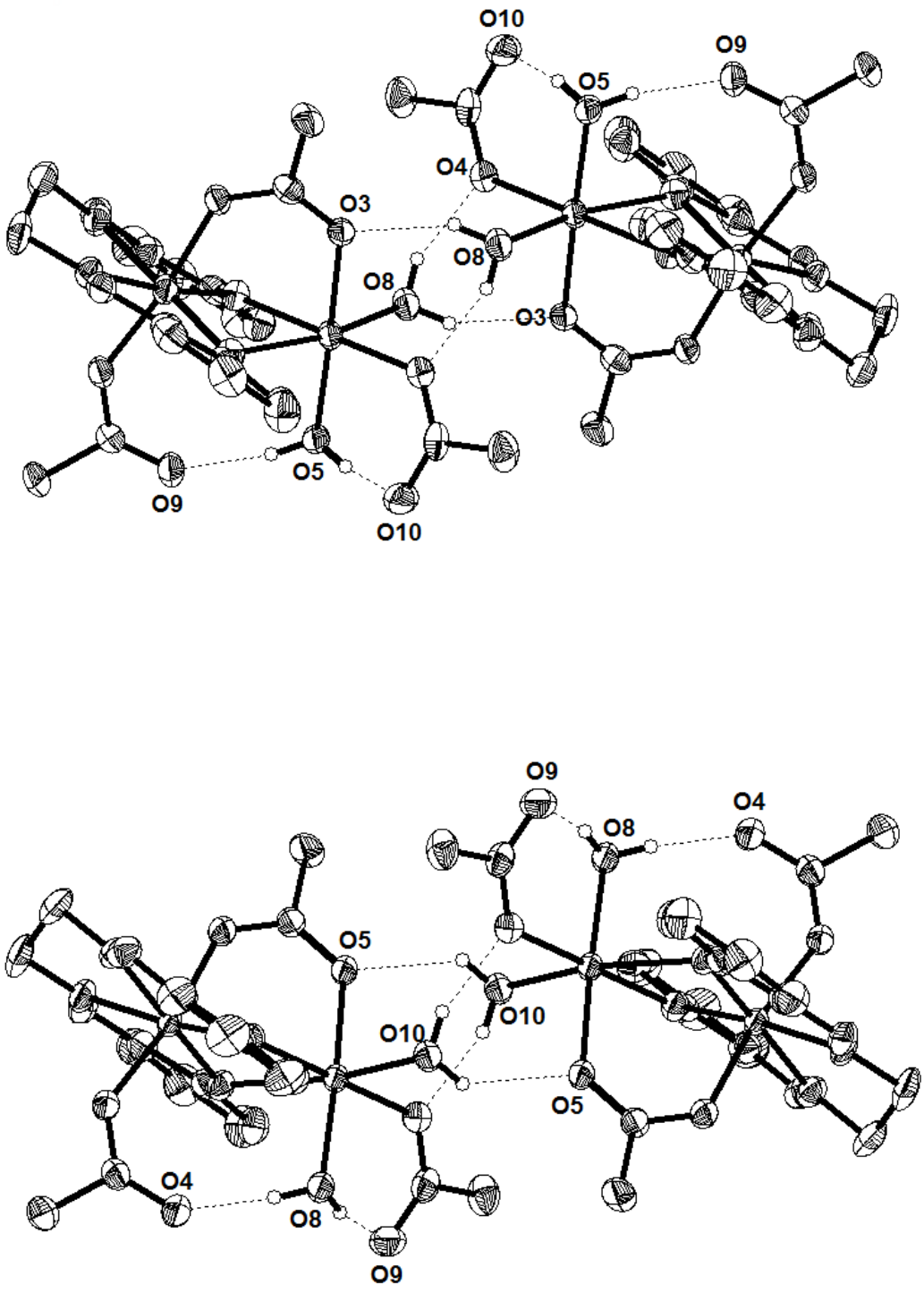


**Figure S3**. *ORTEP* representation of complexes **2** (top) and **3** (bottom) showing H-interactions between closest neighbours. Ellipsoid probability: 50%. Hydrogen atoms and *tert*-butyl groups have been omitted for clarity.

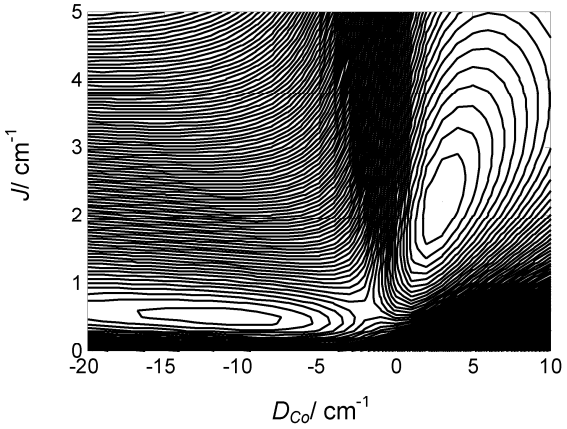


**Figure S4**. Contour error plot of correlated $J - D_{Co}$ parameters for $\chi T$ *vs. T* simulation plot of complex **3** with Hamiltonian of Eq.2+zfs (see text).

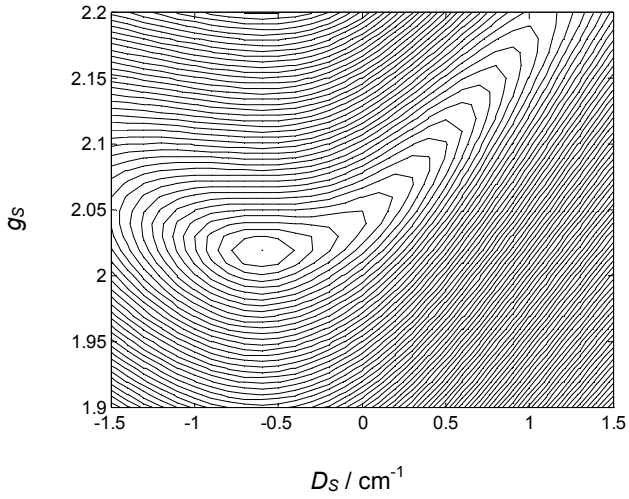


**Figure S5**. Contour error plot of correlated $g_S - D_s$ parameters for *M vs. (H/T)* simulation plots of complex **2** with Hamiltonian of Eq.4 (see text).

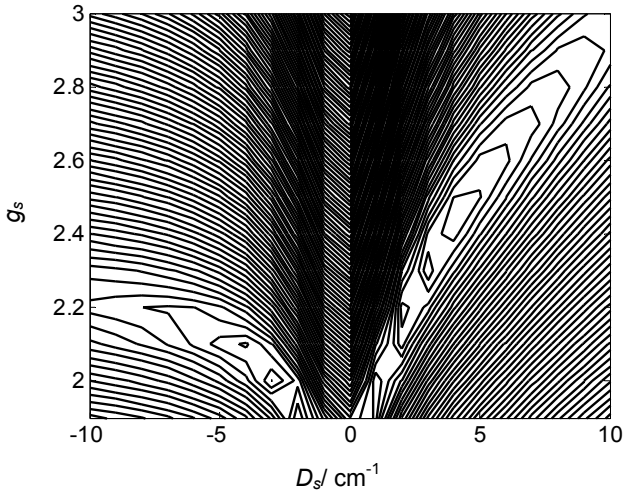


**Figure S6**. Contour error plot of correlated $g_S - D_s$ parameters for *M vs. (H/T)* simulation plots of complex **3** with Hamiltonian of Eq.4 (see text).

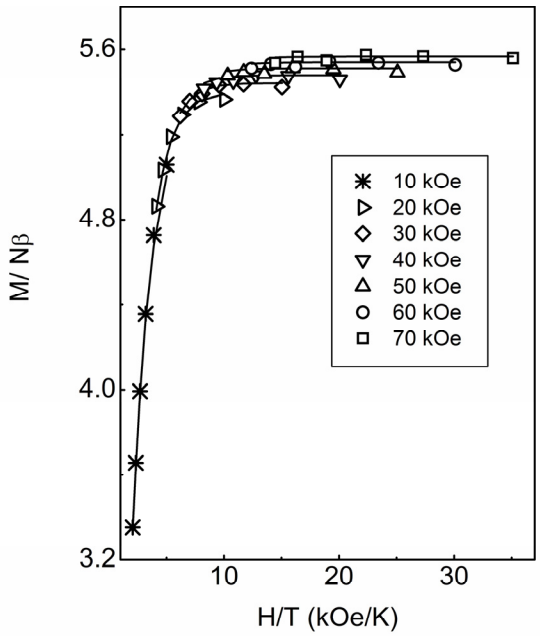


**Figure S7**. Plot of reduced magnetization (*M/Nβ*) *vs. H/T* for a non-restrained sample of complex **3** in the 2-5 K range. The solid lines are the fitting of the data with Hamiltonian of Eq. 4 (see text) for a specific sample orientation with respect to field.

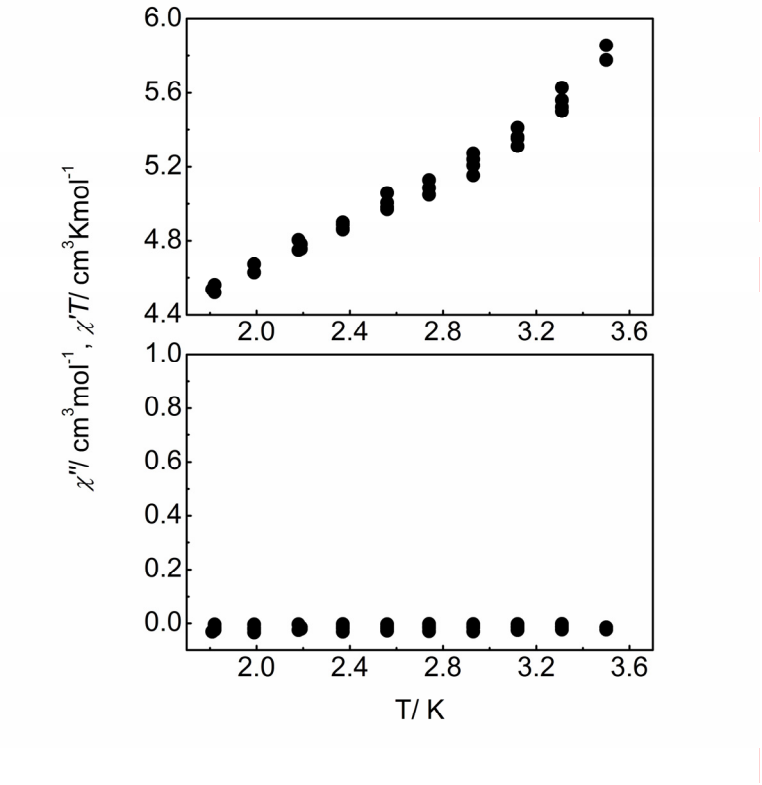


**Figure S8**. Plot of $\chi'T$ *vs. T* (top) and $\chi''$ *vs. T* (bottom) for complex **3** at different driving AC frequencies under 0 DC external field.

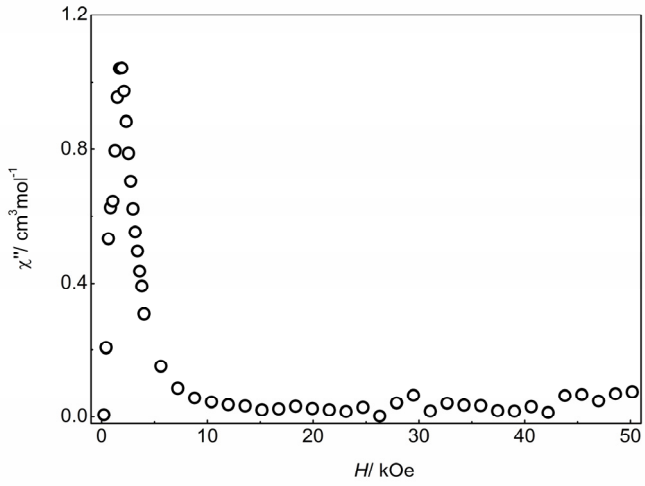


**Figure S9**. Plot of $\chi''$ *vs.* external DC field for complex **3**, at 1.8 K with a 1500 Hz driving AC frequency.

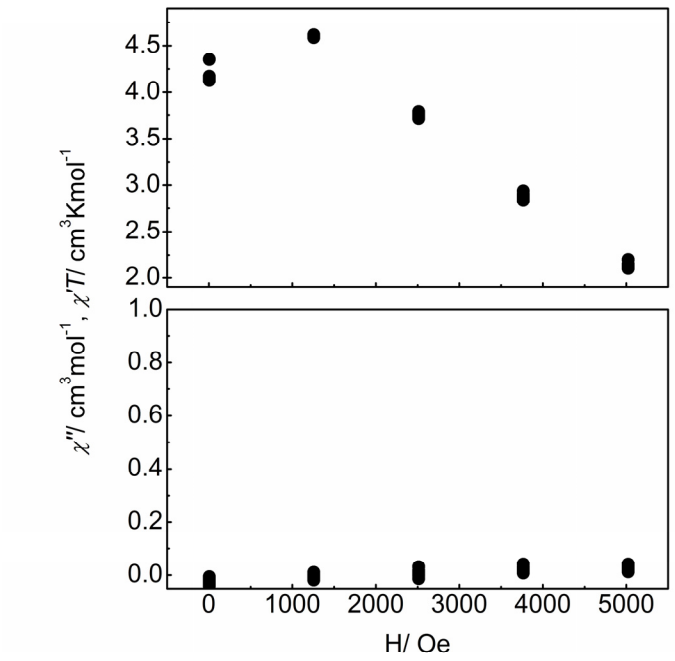


**Figure S10**. Plot of $\chi'T$ *vs. H* (top) and $\chi''$ *vs. H* (bottom) at 1.8 K for complex **2** at different driving AC frequencies (up to 1500 Hz).