Supplementary Material (ESI) for Dalton Transactions

ELECTRONIC SUPPORTING INFORMATION

Using pyridine amidoximes in 3d-metal cluster chemistry: a novel ferromagnetic Ni_{12} complex from the use of pyridine-2-amidoxime

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Single-crystal X-ray diffraction

A suitable single-crystal of $[Ni_{12}\{(py)C(NH)NO\}_6\{(py)C(NH_2)NO\}_6Cl_2(MeOH)_2]Cl_4\cdot 5MeOH$, was mounted on a Hampton Research CryoLoop using FOMBLIN Y perfluoropolyether vacuum oil (LVAC 25/6) purchased from Aldrich,[1] with the help of a Stemi 2000 stereomicroscope equipped with Carl Zeiss lenses. Data were collected at 150(2) K on a Bruker X8 Kappa APEX II charge-coupled device (CCD) area-detector diffractometer (Mo K_α graphite-monochromated radiation, $\lambda = 0.71073$ Å) controlled by the APEX2 software package,[2] and equipped with an Oxford Cryosystems Series 700 cryostream monitored remotely using the software interface Cryopad.[3] Images were processed using the software package SAINT+,[4] and data were corrected for absorption by the multi-scan semi-empirical method implemented in SADABS.[5] The structure was solved by the direct methods of SHELXS-97,[6] and refined by full-matrix least squares on F^2 using SHELXL-97.[7] All non-hydrogen atoms were directly located from difference Fourier maps and successfully refined with anisotropic displacement parameters. Hydrogen atoms associated with the nitrogen atoms were markedly visible in difference Fourier maps and were included in the structure with the N–H and H···H distances restrained to 0.90(1) and 1.50(1) Å, respectively, and with $U_{iso} = 1.5\times U_{eq}(N)$. Three uncoordinated crystallographically independent methanol moieties were directly located from difference Fourier maps, totally adding up to 5 molecules per unit cell (one is half occupied). Hydrogen atoms attached to carbon and to the hydroxyl groups were located at their idealised positions and included in the structural model in subsequent refinement cycles in riding-motion approximation with $U_{iso} = 1.2$ (aromatic carbon) or 1.5 ($–CH_3$ and –OH groups) of U_{eq} of the parent atom. A considerable smeared-out electron density was found in the empty spaces available in the structure which prevented a sensible location and refinement of additional solvent molecules. Searches for the total potential solvent area using the software package *PLATON*[8] revealed the presence of a large cavity centered at (½ ½ ½) with an internal volume of *ca.* 418 Å^3 (*ca.* 15% of the total volume of the unit cell). The original data set was then mathematically treated

using the *SQUEEZE*[9] subroutines in order to remove the contribution of these highly disordered molecules in the solvent-accessible volume. It was estimated that the *ca.* 15% empty volume would contain *ca.* 181 electrons. Taking into consideration that small solvent molecules should occupy in average *ca.* 40 Å^3, it is thus feasible to assume that approximately 10 additional methanol molecules are still located in the empty spaces of the structure (*i.e.*, $n \approx 10$). The calculated solvent-free reflection list was than used for further structural refinement.

Crystal data: $C_{79}H_{94}Cl_6\ N_{36}Ni_{12}O_{19}$, $M = 2769.12$, triclinic, space group $P\bar{1}$, $Z = 1$, $a = 14.8718(8)$ Å, $b = 15.1738(7)$ Å, $c = 15.3809(8)$ Å, $\alpha = 60.525(2)^\circ$, $\beta = 73.084(3)$, $\gamma = 69.854(2)^\circ$, $V = 2805.3(3)$ Å^3, μ(Mo-Kα) = 2.182 mm^{-1}, $D_c = 1.639$ g cm^{-3}, brown prisms with crystal size of 0.20×0.18×0.09 mm^3. Of a total of 147901 reflections collected, 14885 were independent ($R_{int} = 0.0422$). Final $R1 = 0.0596$ [$I > 2\sigma(I)$] and $wR2 = 0.2006$ (all data). Data completeness to theta = 29.13°, 98.6%. CCDC 678537. *Crystal data for squeezed structure*: Final $R1 = 0.0412$ [$I > 2\sigma(I)$] and $wR2 = 0.1257$ (all data). CCDC 678538.

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