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ESRF

Experiment Report Form

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Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

ESRF	**Experiment title:** Experimental vs theoretical studies on the electron density of some S-bridged manganese complexes.	**Experiment number**: 01-02-673
Beamline: BM1A	**Date of experiment**: from: 29/6/2005 to: 2/7/2005	**Date of report**: 10/1/2006 *Received at ESRF:*
Shifts: 12	**Local contact(s)**: Philip Pattison	

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Report:

Introduction

Although a very rich literature exists involving theoretical calculations on structure and bonding for transition-metal carbonyl complexes, very few theoretical studies have been made to date for metallic polysulfides and other related compounds. In earlier works (see Refs [1]-[6]) we gave the results of some *ab initio* calculations performed on Mn and Ru mono-, bi- and trinuclear carbonyl complexes, including some highly electrophilic carbenes, in order to obtain their theoretical geometries, as well as some electronic properties, and compare them with those found by standard X-ray diffraction methods. Those works were a first step to a more complete experimental and theoretical characterization of chemical bonds and interesting non-bonding interactions in these complexes that we are now trying to accomplish. The main aim of the present work was to obtain high-quality and low-temperature data sets for some S- and Se-bridged manganese complexes, as well as for other related compounds, using synchrotron radiation in order to extract their experimental electron densities from a multipole refinement procedure and compare them with theoretical calculations made at the *ab initio* level by using density functional theory methods. Electron density properties, and in particular the bond related topological properties, will be explored from the theoretical and experimental electron density maps.

Experiments description

Experiments started at 8:00 am on Wednesday 29/6/05 and ended at 8:00 am on Sunday 3/7/05 at SNBL. Data collection was made by using a KUMA KM6-CH (equipped with a CCD detector) six-circle κ single-crystal diffractometer as a standard four-circle instrument. The data collection temperature, controlled by an Oxford cryostream cooling system, was 100 K, and the wavelength of the radiation used was 0.71 Å. Four different samples, corresponding to four different compounds already measured at home in our laboratory, were used during the four days, but the experimental strategy was similar in all the four cases: (1) a good diffracting crystal was selected (the crystal was mounted on the diffractometer and a couple of frames were observed prior to start the complete data collection); (2) around 20 frames were collected for indexing purposes; (3) a run of about 2 h of data collection was then used to try to solve the structure; (4) finally, the full data set was collected. In fact, three different data sets were collected at this stage for each of the four samples: a high angle data set, using no filter, was collected first; then a low angle data set was collected using a 50 µm Cu filter, and finally a very low angle data collection was performed with a 100 µm Cu filter. Data reduction was then applied using the XD_RED program, and absorption corrections were also applied by using SADABS. Solution and preliminary standard refinements were made *in situ* at SNBL for the first three samples by using the WinGX program package. Some details of the data collected for the four different samples are as follows:

1) Code: MV-S_2H_2. After an unsuccessful try, a good crystal was used for collecting data (see Fig. 1). The cell parameters found were: a = 17.071(1) Å, b = 17.699(1) Å, c = 23.474(1) Å, α = 90.040(5)°, β = 93.683(6)°, γ = 89.953(6)° (Z = 4, space group $P2_1/n$). Molecular formula: $[Mn(CO)_4(PPh_2)_2CH\text{-}S\text{-}S\text{-}CH(PPh_2)_2(CO)_4Mn](ClO_4)_2 \cdot HClO_4 \cdot 2CH_2Cl_2 \cdot 3H_2O$. Other data for this sample are included in Table I.

2) Code: MV-Se_2H_2. A picture of the selected crystal may be seen in Fig. 2. The cell parameters found were: a = 11.7436(7) Å, b = 15.577(1) Å, c = 20.565(1) Å, α = 70.064(6)°, β = 82.419(5)°, γ = 68.787(6)° (Z = 2, space group $P\bar{1}$). Molecular formula: $[Mn(CO)_4(PPh_2)_2CH\text{-}Se\text{-}Se\text{-}CH(PPh_2)_2(CO)_4Mn](ClO_4)_2 \cdot 2CH_2Cl_2$. Other relevant data for this compound are included in Table I.

3) Code: Zn_2. The successful crystal mounted on the goniometer head is shown in Fig. 3. The cell parameters found were: a = 6.9115(6) Å, b = 10.889(1) Å, c = 13.893(1) Å, α = 109.91(1)°, β = 101.551(8)°, γ = 93.905(9)° (Z = 2, space group $P\bar{1}$). Molecular formula: $(CH_3C)_5Zn\text{-}Zn(CCH_3)_5$. Other relevant data are included in Table I.

4) Code: Ru_3. A previous attempt with a related osmium compound was unsuccessful due to the tiny crystals available. On the other hand, good crystals were available for the ruthenium compound. The cell parameters found for this compound were: a = 10.372(1) Å, b = 9.8453(7) Å, c = 18.668(2) Å, β = 96.109(9)° (Z = 4, space group $P2_1/c$). Molecular formula: $Ru_3(CO)_9H_2CH(C_3H_2N_2CH_3)$. An ORTEP plot for this complex is shown in Fig. 4. Other relevant data are included in Table I.

Fig. 1. The Mn(S-S) crystal.

Fig. 2. The Mn(Se-Se) crystal.

Fig. 3. The Zn-Zn crystal.

Table I. Data collections for the four samples.

	MV-S_2H_2	MV-Se_2H_2	Zn_2	Ru_3
No. Reflections measured	126214	223014	57015	117474
No. Reflections unique	18799	49017	13873	17706
R_{int}	0.0890	0.0438	0.0561	0.0574
R_σ	0.0357	0.0277	0.0315	0.0315
$(\sin \theta/\lambda)_{max}$ (Å^{-1})	1.41	1.08	1.08	1.08
F(000)	3344	1628	420	1352
μ (mm^{-1})	0.77	1.89	2.51	2.43
ρ (g cm^{-3})	1.54	1.64	1.40	2.48

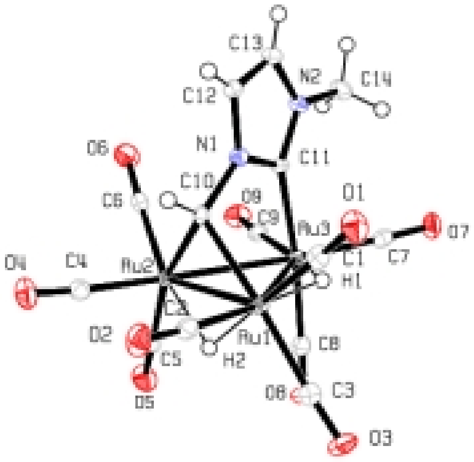

Fig. 4. The Ru_3 compound.

References

[1] Van der Maelen, J. F., Ardura, D., García-Granda, S., and Cabeza, J., *Acta Cryst.* **1996**, A52, C304.

[2] Ruiz, J., Ceroni, M., Quinzani, O. V., Riera, V., Vivanco, M., García-Granda, S., Van der Maelen. J. F., Lanfranchi, M., and Tiripicchio, A., *Chem. Eur. J.* **2001**, 7, 4422-4430.

[3] Van der Maelen, J. F., García-Granda, S., and Ruiz, J., *Acta Cryst.* **2002**, A58, C88.

[4] Van der Maelen, J. F., Ruiz, J., and García-Granda, S., *J. Appl. Cryst.* **2003**, 36, 1050-1055.

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[6] Van der Maelen, J. F., Ruiz, J., and García-Granda, S., *J. Theor. Comput. Chem.* **2005**, 4, 823-832.