

Further Structural Information on the Intra- and Interunit Contacts in Dimeric Ruthenium Phthalocyanine

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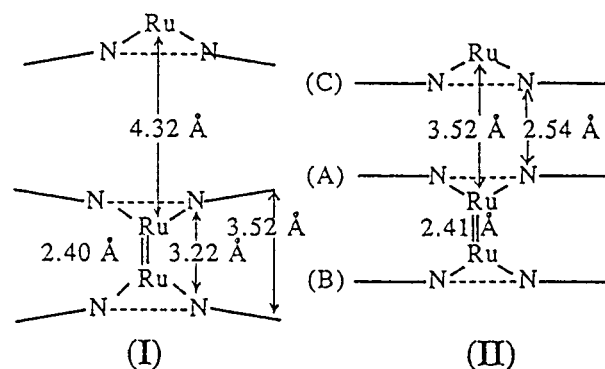
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Previous EXAFS and further LAXS studies fully confirm that solid amorphous ruthenium phthalocyanine, as obtained from its DMSO, pyridine, and isoquinoline adducts, is dimeric with dimers chained to form aggregates of formula [(PcRu)₂]_n (average *n* = 6) and with short intradimer Ru–Ru (2.40 Å) and long interdimer (4.30–4.40 Å) bond distances, in contrast with recent different EXAFS findings (very short Ru–Ru interdimer contacts, 3.52 Å) and an associated structural model.

Introduction

Ruthenium phthalocyanine was recently shown by the LAXS technique to consist of dimeric units, (PcRu)₂, internally held together by a direct Ru–Ru bond (2.40 Å) and linearly chained to give an aggregate of formula [(PcRu)₂]_n (average *n* = 6) (I) with the examers disorderly arranged in the solid amorphous material.¹ In a MO approach, the couple of Ru atoms (d¹²) within the dimer was assigned the electronic structure $\sigma^2\pi^4\delta^2\delta^*2\pi^*2$ in keeping with the presence of a clean Ru(II)=Ru(II) double bond. Interpretation of the magnetic data clearly explains the strong intradimer Ru–Ru spin–spin coupling, occurring as a function of the temperature in the absence of significant magnetic metal–metal interdimer contacts (Ru–Ru distance 4.32 Å). The semiconducting properties of the material could be accounted for in terms of the π – π interaction between adjacent macrocycles within the stacked assemblies formed by the dimeric units. Three different adducts have been reported, i.e., [PcRu(DMSO)₂]·2DMSO,^{2a} PcRu(py)₂, and PcRu(qnl)₂ (recently reformulated as PcRu(iqnl)₂),^{2b} from which (PcRu)₂ is commonly obtained as an amorphous material by thermal treatment under vacuum. We could ascertain by X-ray powder and LAXS spectra³ (see Figures 1 and 2) that the solid species obtained from all the adducts are practically undistinguishable. Recently,⁴ the EXAFS spectrum of (PcRu)₂ was reported, and as shown in columns 1 and 2 of Table 1, the relevant intra- and interdimer bond distances appeared to indicate quite a satisfactory agreement between the LAXS¹ and EXAFS⁴ structural data. The comparison is obviously only confined to those distances that the EXAFS technique is able to explore.



In a more recent paper, Bertagnolli et al.,⁵ apparently unaware of the previous EXAFS report,⁴ had examined again the EXAFS spectrum of (PcRu)₂. These authors, referring exclusively to our previous LAXS data,¹ confirm the dimeric structure of the complex (Table 1, column 3). However, they report a value of 3.52 Å for the Ru–Ru interdimer distance, quite different from that proposed by us previously (4.32 Å)¹ and from the analogous value (4.42 Å) derived from the previous EXAFS spectrum.⁴ The observed short Ru–Ru interdimer distance seems to be capable of substantially modifying the type of interdimer contacts with respect to our proposed model. This point will be briefly discussed below.

Experimental Section

Our X-ray powder and LAXS spectra were taken on the same samples that were still available since our first publication on the matter. The LAXS technique and operative conditions for the collection of data were identical to those given elsewhere.^{1,3}

Results and Discussion

Bertagnolli's model (Figure 2 in ref 5, see also II) implies that the two (planar) Pc units within the dimer are located at a distance of 3.39 Å. Internally, consequent to out-of-plane

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(1) Capobianchi, A.; Paoletti, A. M.; Pennesi, G.; Caminiti, R.; Ercolani, C. *Inorg. Chem.* **1994**, *33*, 4635. Abbreviations used in the present paper: Pc = phthalocyaninato anion, C₃₂H₁₆N₈²⁻; DMSO = dimethyl sulfoxide; py = pyridine; qnl = quinoline; iqnl = isoquinoline.

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(3) Capobianchi, A.; Pennesi, G.; Paoletti, A. M.; Caminiti, R.; Sadun, C.; Ercolani, C. *Inorg. Chem.* **1996**, *35*, 4643.

(4) Alagna, L.; Capobianchi, A.; Pennesi, G.; Prosperi, T.; Rossi, G. *J. Phys. IV* **1997**, *C2*, 1261.

(5) Bertagnolli, H.; Weber, A.; Hörner, W.; Ertel, T. S.; Reinöhl, U.; Hanack, M.; Hees, M.; Polley, R. *Inorg. Chem.* **1997**, *36*, 6397.

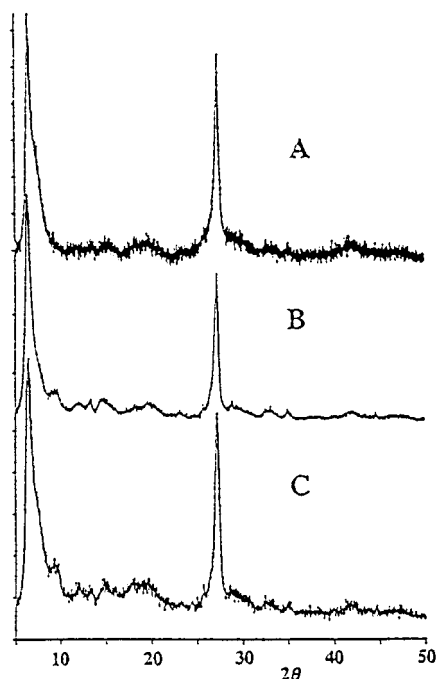


Figure 1. X-ray powder spectra of ruthenium phthalocyanine: (A) sample obtained from the DMSO adduct; (B) sample from the py adduct; (C) sample from the iqnl adduct.

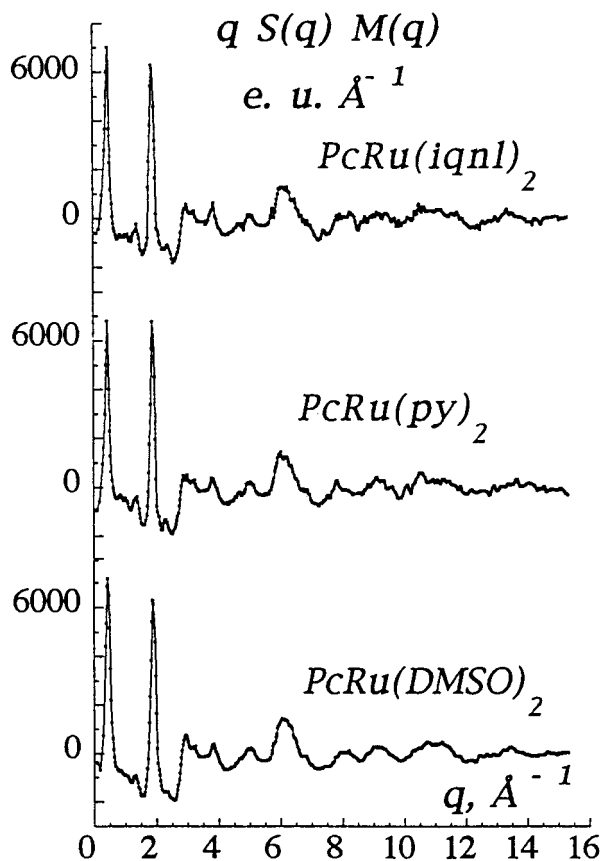


Figure 2. Experimental structure-function of ruthenium phthalocyanine as obtained from the different adducts.

displacement of both Ru(A) and Ru(B) atoms by 0.49 Å from each respective Pc(A) and Pc(B) unit the fixed Ru–Ru bond distance is 2.41 Å, which is in good agreement with previous data.^{1,4} In the same model, if the Ru(C) atom of the adjacent dimer is 3.52 Å and, again, 0.49 Å from the respective Pc(C) unit, the distance between Pc(A) and Pc(C) is easily calculated

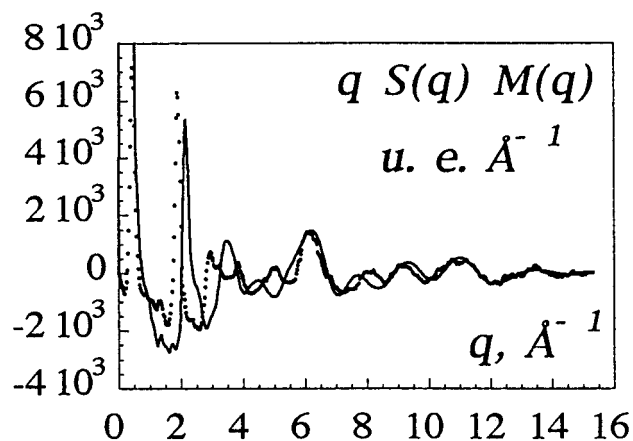


Figure 3. Observed (···) and calculated (—) $q S(q) M(q)$ values vs $q = (4\pi/\lambda)(\sin \theta)$ (see ref 1).

Table 1. Selected Intra- and Interdimer Bond Distances (Å) for (PcRu)₂

	LAXS	EXAFS (ref 4)	EXAFS (ref 5)
Ru(A)–N(A)	1.97	1.98	2.03
Ru(A)–Ru(B)	2.40	2.38	2.41
Ru(A)–C(A)	2.96	3.01	3.03
Ru(A)–N(A)	3.35	3.26	3.21
Ru(A)–N(B)	3.40		3.37
Ru(A)–Ru(C)	4.32	4.42	3.52

as 2.54 Å, almost 1 Å shorter than the intradimer Pc(A)–Pc(B) distance, and far too short for a contact justified only by the Wan der Waals interactions. Indeed, such a distance has never been observed even in bis-phthalocyanine sandwich-type molecules (>3.00 Å),⁶ including those in which the strong attraction by the metal center links together the two Pc units by C–C σ bonds (3.08 Å)⁷ or in partially oxidized linearly aggregated metal phthalocyanine units, where the short π – π contacts (3.1–3.2 Å) between adjacent molecules generates electrical conduction.⁸ In light of this, the Ru–Ru interdimer distance of 3.52 Å appears questionable. Noticeably, such a distance would probably imply some kind of magnetic superexchange for the Ru atoms along the aggregated dimers; however, no trace of such a type of exchange has been found in our detailed magnetic investigation.¹ Clearly, the discrepancy about the reported interdimer contacts⁵ with respect to our LAXS¹ and previous EXAFS data⁴ needed to be considered. Preliminarily, we were informed⁹ that a careful reexamination of the EXAFS spectrum of (PcRu)₂ definitely confirmed previously published data,⁴ with only nonrelevant changes for the complete set of distances given. To further test the model proposed by Bertagnoli et al., we have also attempted a fitting of the experimental static structure function by assuming the structural features shown in **II** with eclipsed and planar Pc units and a molecular aggregation reasonably chosen to correspond on average to six dimers, as in our model. Figures 3 and 4 show, respectively, the experimental $q S(q) M(q)$ and Diff(r) and the calculated functions. The curves in Figure 3 show a good correspondence in the region above 5 Å⁻¹ (intradimer short distances) but significant differences in the peak positions in

(6) Koike, N.; Uekusa, H.; Ohashi, Y.; Harnoo, C.; Kitanura, F.; Osaka, T.; Tokuda, K. *Inorg. Chem.* **1996**, *35*, 5798 and references therein.

(7) Donzello, M. P.; Ercolani, C.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1998**, *37*, 1347.

(8) Capobianchi, A.; Ercolani, C.; Paoletti, A. M.; Pennesi, G.; Rossi, G.; Chiesi-Villa, A.; Rizzoli, C. *Inorg. Chem.* **1993**, *32*, 4605 and references therein.

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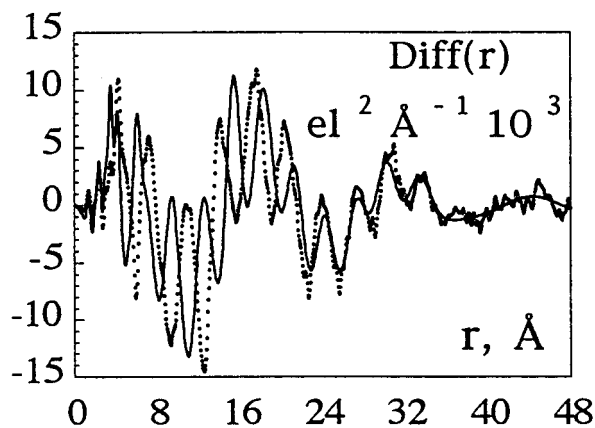


Figure 4. Experimental function $\text{Diff}(r) = D(r) - 4\pi r^2 \rho$ (···) and the calculated function (—) (see ref 1).

the region $0.5\text{--}5 \text{ \AA}^{-1}$ (intra- and interdimer long distances). Corresponding differences are clearly observed in the $\text{Diff}(r)$ functions (Figure 4), which show quite an unsatisfactory correspondence of experimental and calculated peak positions in the region above 3.5 \AA . No significant improvement in the fitting is observed by allowing the Pc units to change their relative position in the range $0\text{--}45^\circ$. On the basis of these

results, we confidently confirm the structural model proposed by us for the solid material $(\text{PcRu})_2^1$ (I). It should be noticed that a similar structural model has been found for the corresponding osmium dimer.¹⁰ Finally, a single-crystal X-ray structural work has been just reported on the phthalocyanine dimer $(\text{PcRe})_2^{11}$ for which intradimer details, i.e., metal–metal bond distances, out-of-plane displacement of metal centers, average Pc–Pc distance, and domed conformation of the Pc units, as well as Pc–Pc and Re–Re interdimer contacts seem to be fully compatible with our structural analysis of both the Ru and Os dimers.

Since the X-ray powder spectrum of the sample of ruthenium phthalocyanine examined by Bertagnolli et al.⁵ is not available, we are unable to compare directly the structural features of that sample with ours. There is little doubt, in our opinion, that any significant difference between the various samples examined might exist.

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(11) Göldner, M.; Hückstädt, H.; Murray, K. S.; Moubaraki, B.; Homborg, H. *Z. Anorg. Allg. Chem.* **1998**, *624*, 288.

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