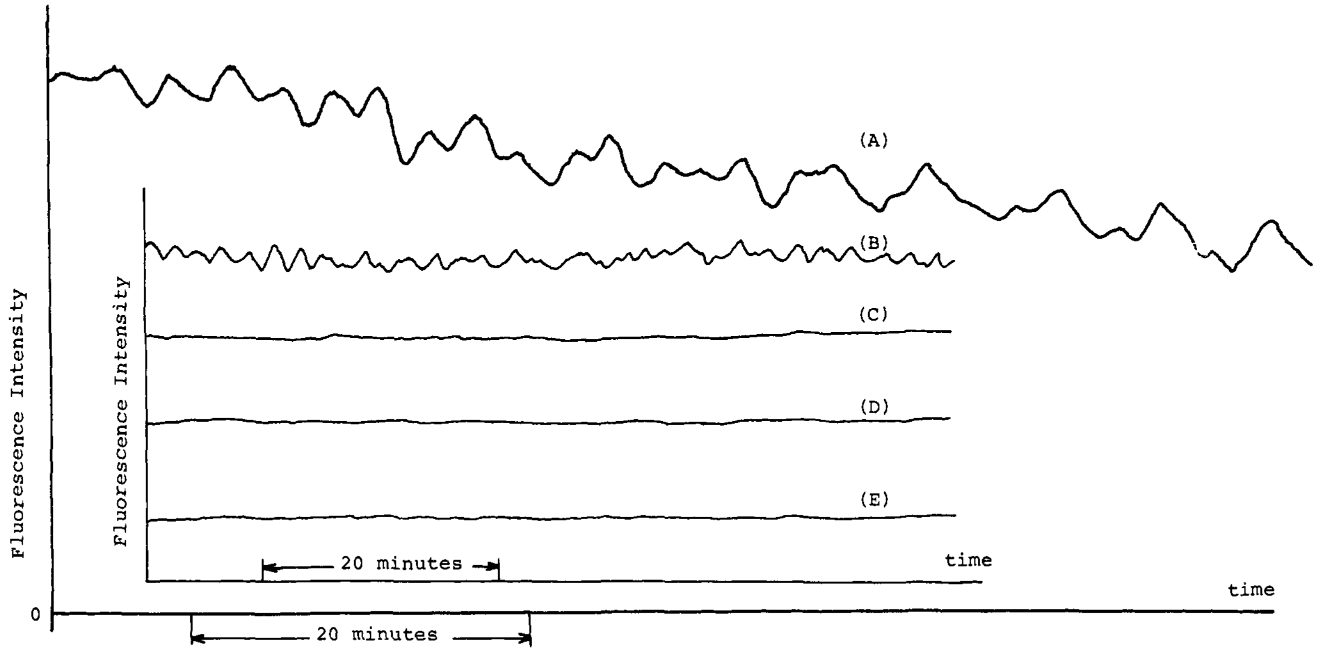

Figure 1. Plots of fluorescence intensity against time at 298 K. (A) Zinc protoporphyrin dimethyl ester in 0.05 M SDS solution. The base line is shown for this line (number 0). (B) Zinc protoporphyrin dimethyl ester in 0.08 M SDS solution. (C) Zinc protoporphyrin dimethyl ester in MeOH. (D) Zinc protophryin dimethyl ester in HTAB solution. (E) Ruthenium tris(bipyridyl) in SDS solution. All curves of zinc protoporphyrin dimethyl ester are for an excitation wavelength of 410 nm and an emission wavelength of 580 nm.

The measurements of fluorescence intensity were performed at several times over a period of 2 weeks because some aging of the micellar solution is necessary to obtain reliable results. Chaotic variations in fluorescence intensity were observed during these experiments, and the overall intensity of absorption in the visible spectrum declined steadily with time. Figure 1 shows typical plots of zinc protoporphyrin fluorescence intensity at 580 nm against time in ~3 mL of SDS micellar solution at 298 K. As the Soret band of zinc protoporphyrin in SDS micelles was observed at 412 nm, the fluorescence was excited at 410 nm during these measurements. Under the usual conditions, chaotic oscillations as shown in Figure 1 were observed. Figure 1 also contains the results in methanol and in hexadecyltrimethylammonium bromide (HTAB) micelles. The variation in fluorescence intensity in the methanol solution was not observed, as shown in Figure 1. In the case of HTAB micelles, the variation was also not observed under the same conditions as those of SDS, but a slight variation was observed when the sample cell was irradiated by a higher intensity of light or the concentration of HTAB was greatly increased. The fluorescence intensity of tris(bipyridyl)ruthenium complex in an SDS micellar system was measured to check the properties of the micellar system employed in this experiment, and no fluctuations were observed in the emission spectrum. In addition, measurements of anthracene in methanol also gave the same results. Thus, the observation about zinc protoporphyrin is real and independent of the source of the instrumentation and of the chemical materials, such as impurity.

In the measurements on the SDS micelles, the overall fluorescence intensity gradually declined and the amplitude of variation increased with time. The rate of decrease increases with an increase in light intensity. However, the period and the pattern of the variation in intensity of fluorescence and the induction time were not always reproducible. When the solution was stirred, the chaotic variation ceased and the intensity increased instantly and then showed a gradual steady decline. However, the variation in intensity commenced again when the stirring was stopped and the solution was quiet. This result may indicate that the variation is dependent on localizations rather than on overall bulk concentrations. This behavior is similar to that of other systems reported already.[3,5] In addition, when a quencher (methylviologen) was added to the SDS solutions, the fluctuations ceased and the overall intensity in fluorescence decreased. The intensity of the Soret band of zinc protoporphyrin in the SDS micellar system is decreased by the irradiation of light for a long time, indicating decomposition of the porphyrin skelton. Though we do not have a detailed interpretation of this observation, the experimental results appear interesting and directly related to the occurrence of chemical instabilities. A detailed analysis of many features of this phenomenon is in progress.

P-450-Type Dioxygen Activation Using H_2/Colloidal Pt as an Effective Electron Donor

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The catalytic cycle of cytochrome P-450, an important heme-containing monooxygenase of liver microsomes, involves the NADH-dependent *reductive dioxygen activation* to give an active oxidizing species having a Fe–O bond.[1] This unique oxidizing species has absorbed increasing attention of chemists. Successful oxygen atom transfer from iodosylbenzene to synthetic iron(III) porphyrins,[2] P-450, or other metal ion porphyrins[3,4] were reported. The reductive dioxygen activation was first modeled by us using a totally artificial system, $NaBH_4$–(tetraphenylporphinato)man-

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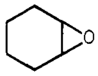
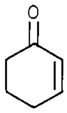
(1) (a) Sato, R.; Omura, T. In "Cytochrome P-450": Kodansha Ltd.: Tokyo, 1978. (b) Boyd, G. S.; Ullrich, V. *Biochem. Soc. Trans.* **1975**, 803. (c) Nordblom, G. D.; White, R. E.; Coon, M. J. *Arch. Biochem. Biophys.* **1976**, *175*, 524. (d) Hrycay, E. G.; Gustafsson, J.; Ingelman-Sundberg, M.; Eruster, L. *Biochem. Biophys. Res. Commun.* **1975**, *66*, 209.

(2) (a) Presented by Groves, J. T. at the American Chemical Society/Chemical Society of Japan Chemical Congress, Honolulu, April 1979. (b) Groves, J. T.; Nemo, T. E.; Myers, R. S. *J. Am. Chem. Soc.* **1979**, *101*, 1032. (c) Chang, C. K.; Kuo, M.-S. *J. Am. Chem. Soc.* **1979**, *101*, 3414. (d) Groves, J. T.; Krichnan, S.; Avaria, G. E.; Nemo, T. E. "Biomimetic Chemistry"; American Chemical Society: Washington, DC, 1980; Adv. Chem. Ser. No. 191.

(3) Groves, J. T.; Kruper, W. J., Jr. *J. Am. Chem. Soc.* **1979**, *101*, 7613.

(4) (a) Hill, C. L.; Schardt, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 6374. (b) Groves, J. T.; Kruper, W. J., Jr.; Hanshalter, R. C. *Ibid.* **1980**, *102*, 6375.

Table I. TPP·Mn$^{\mathrm{III}}$ Catalyzed Oxidation of Cyclohexene[a]

ligand	reaction time, h	 yield, 10^{-5} mol (%)	 yield, 10^{-5} mol^{b,c} (%)
imidazole[d]	14	16.1 (1130)	0.8 (60)
2-methylimidazole[d]	14	25.7 (1810)	2.0 (140)
1-methylimidazole[d]	14	55.8 (3920)	3.7 (260)
1-methylimidazole	63	91.9 (6470)	6.3 (440)

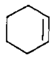
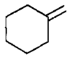
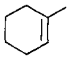
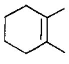
[a] Reaction conditions were shown in the text. [b] Cyclohexenol was also obtained in less than 10^{-6} mol. [c] Yields in parentheses based on TPP·Mn$^{\mathrm{III}}$, %. Yield of cyclohexene oxide based on H_2 and O_2 was 2.1 and 4.3%, respectively, for 5 h of reaction time. [d] Average of three experiments. In the absense of imidazole, total products obtained were less than 3×10^{-6} mol after 5 h of reaction time.

ganese(III) (abbreviated as TPP·Mn$^{\mathrm{III}}$)–O_2,[5,6] which corresponds closely to the native NADH–hemoprotein–O_2 system. This artificial system catalyzed the epoxidation of cyclohexene efficiently.

However, the system $NaBH_4$–TPP·Mn$^{\mathrm{III}}$–O_2 did not give direct oxygenation products but those after further reduction with $NaBH_4$, and we have been making extensive investigations to determine a system for direct oxygenation. Now we wish to report a new system giving direct oxygenation products by using dihydrogen as an electron donor.

As reported previously, in the presence of an appropriate electron donor, TPP·Mn$^{\mathrm{III}}$ is converted to TPP·Mn$^{\mathrm{II}}$ which activates dioxygen to form a powerful oxidizing species. Now we found that colloidal platinum efficiently catalyzed electron transfer from H_2 to TPP·Mn$^{\mathrm{III}}$ to form TPP·Mn$^{\mathrm{II}}$. A 1.2×10^{-5} M solution of TPP·Mn$^{\mathrm{III}}$ in benzene–ethanol saturated with H_2 gave TPP·Mn$^{\mathrm{II}}$ instantaneously ($\tau_{1/2} < 5$ s) by the addition of colloidal Pt (3×10^{-8} g equiv). We replaced $NaBH_4$ by this new electron-donating system in the P-450 model. Thus, colloidal Pt (3.0×10^{-6} g equiv Pt), prepared by a modification of the procedure reported by Hirai[7] and suspended in 1 mL of ethanol, TPP·Mn$^{\mathrm{III}}$Cl[8] (1.4×10^{-5} mol), imidazole (3.7×10^{-4} mol), and cyclohexene (4.9×10^{-3} mol) were mixed with 2 mL of benzene, and the resultant solution was stirred vigorously under H_2–O_2 (1:1 vol/vol) mixed gas in the dark. After 14 h a very small amount of water separated, when the organic phase was analyzed by means of GLC and IR spectroscopy. Cyclohexene oxide was detected as a major product. 3-Cyclohexenone and a very small amount of 3-cyclohexenol were also produced, but no detectable amount of cyclohexanol was formed (Table I). Under the optimal conditions, (run 4, Table I), yield of cyclohexene oxide reached 29 400% based on Pt, 6470% based on TPP·Mn$^{\mathrm{III}}$, and 240% based on 1-methylimidazole after 63 h when precipitation of Pt was observed. This good turnover indicates that each component involved acts as a real catalyst. The observations that no appreciable epoxidation took place when one of the components (Pt, H_2, TPP·Mn, O_2) was omitted also supports the significance of every catalyst involved. Thus, the present system of H_2–colloidal Pt–TPP·Mn–O_2 afforded direct oxygenation products efficiently and in high yield, without serious perturbation by autoxidation or further reduction.[9] An alternative that H_2 and O_2 might produce H_2O_2 under the present catalytic conditions as a real oxygenation reagent was excluded because of the finding that H_2O_2 was only produced, if any, in less than 1×10^{-7} mol under conditions listed in Table I (14 h).

Table II. Relative Reactivities of Olefins in the Cytochrome P-450 Model Oxygenation Using TPP·Mn$^{\mathrm{III}}$

olefin	relative reactivity[a]	
	H_2/colloidal Pt–O_2	PhIO[b]
	1	1
	<0.05	<0.05
	0.09	0.09
	0.88	0.96
	0.24	0.23
	1.4	1.3
	1.4	1.3

[a] An equimolar (2.5×10^{-3} mol each) mixture of cyclohexene and the other olefin was oxygenated in the benzene (2 mL)–EtOH (1 mL) containing 3.7×10^{-4} mol of 1-methylimidazole and 1.4×10^{-5} mol of TPP·Mn$^{\mathrm{III}}$Cl. [b] PhIO, 1.8×10^{-4} mol.

Contrary to the smooth epoxidation of olefins the oxygenation of alkanes with the present system proceeded more slowly under the present conditions. Adamantane (2.5×10^{-3} mol) was oxidized to produce 1-adamantanol (44×10^{-6} mol) as a major product together with 2-adamantanol (5×10^{-6} mol) and 2-adamantanone (3×10^{-6} mol) after 14 h. The kinetic isotope effect for the bridgehead hydrogen of adamantane was measured by using 1,3-dideuterated adamantane ($D_2 > 98\%$)[10] as a substrate, and k_H/k_D was determined by means of GC–MS to be 3.3.

The relative reactivity of tertiary to secondary hydrogen of adamantane was ca. 16.5, after statistical correction for the number of hydrogen atoms, in an interesting contrast to the value between 3.8 and 5.4[11] for simple free radical H abstractions and close to (although somewhat smaller than) that observed for TPP·Fe–PhIO.[2b] This high tertiary reactivity strongly suggests that the present oxygenation proceeds either by an electrophilic nonradical intermediate or by a radical species which is abnormally electron deficient.

That the present oxygen transfer proceeds in a concerted fashion is strongly suggested by the stereospecificity observed for *trans*- and *cis*-2-octene where the corresponding epoxide alone was obtained, in an interesting contrast to the epoxidation of stilbene by the TPP·Mn–PhIO system.[4b]

That the present oxidizing species is strongly electrophilic is further supported by the relative reactivities of olefins. The relative reactivities of olefins toward the present H_2–TPP·Mn–O_2 system was estimated from a series of competition experiments, as shown in Table II. The present relative reactivities closely resemble those by TPP·Mn$^{\mathrm{III}}$–PhIO reagent. The present relative reactivity increases with an increase in the number of alkyl substituents (up to three) attached to a double bond (Table II). The relative reactivity is also very sensitive to steric requirement and a transition state seems highly symmetrical (two C–O bond formations take place almost simultaneously). The serious steric hindrance is also seen for 2-octene where trans to cis reactivity ratio (1:10) is very favorable for *cis*-2-octene, in good agreement with TPP·Mn$^{\mathrm{III}}$–PhIO system[4b] (Table II).

No characteristic absorption of an intermediate species (other than TPP·Mn$^{\mathrm{III}}$ and TPP·Mn$^{\mathrm{II}}$) was observed during the reaction, demonstrating that the intermediate species is highly reactive.

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(6) Tabushi, I.; Koga, N. *J. Am. Chem. Soc.* **1979**, *101*, 6456.

(7) Hirai, H.; Nakao, Y.; Toshima, N. *J. Macromol. Sci.-Chem.* **1979**, *A13*, 727.

(8) Kobayashi, H.; Yanagawa, Y. *Bull. Chem. Soc. Jpn.* **1972**, *45*, 450.

(9) Group 8 metal hydride formed by the action of H_2 activates O_2 to oxidize organic compounds. See: James, B. R. In "Biomimetic Chemistry"; Dolphin, D., McKenna, C., Murakami, Y., Tabushi, I., Eds.; American Chemical Society: Washington, DC, 1980; *Adv. Chem. Ser.* No. 191, pp 253–276.

(10) (a) Adamantane-1,3-d_2 was prepared by tri-*n*-butylstannous chloride–$LiAlD_4$ reduction of 1,3-dibromoadamantane.[b] (b) Whitlock, H. W., Jr.; Siefken, M. W. *J. Am. Chem. Soc.* **1968**, *90*, 4929.

(11) Tabushi, I.; Hamuro, J.; Oda, R. *J. Am. Chem. Soc.* **1967**, *89*, 7127.

In summary, a strongly electron-deficient and sterically hindered TPP Mn–O intermediate was produced in the present *reductive* dioxygen activation system which is most probably identical with that obtained from the O-transfer reaction in TPP·Mn^{III}–PhIO system. Further studies directed to the clarification of the reductive oxygen activation mechanism and the identification of active oxidizing species are in progress.

Ordered Magnetic Bimetallic Chains: A Novel Class of One-Dimensional Compounds

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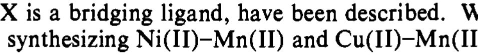
The synthesis and the study of polymetallic complexes, including one-dimensional systems, has been one of the most active fields of inorganic chemistry in the past few years.[1] Surprisingly, till now, no structurally ordered bimetallic chains of the type (A–X–B–X–)$_n$, where A and B are two different paramagnetic metal ions and X is a bridging ligand, have been described. We succeeded in synthesizing Ni(II)–Mn(II) and Cu(II)–Mn(II) compounds of this kind with dithiooxalate as a bridging ligand.

In a previous note[2] we described the crystal structure of $NiZn(S_2C_2O_2)_2(H_2O)_{2.08}$. This compound exhibits a molecular structure made of "infinite" parallel straight chains



in which Ni, Zn, and dithiooxalate groups form planar ribbons, the coordination of all Zn atoms and of a few Ni atoms being octahedrally completed with water molecules.[3]

We report here on the crystal structures and magnetic properties of the Ni(II)–Mn(II)– and Cu(II)–Mn(II)–dithiooxalato systems.[4]

Single crystals of $NiMn(S_2C_2O_2)_2(H_2O)_{7.5}$ (**1**) and $CuMn(S_2C_2O_2)_2(H_2O)_{7.5}$ (**2**) suitable for X-ray analysis were obtained by slowly cooling aqueous solutions of potassium bis(dithiooxalato)nickelate, $K_2Ni(S_2C_2O_2)_2$, or -cuprate, $K_2Cu(S_2C_2O_2)_2$, and manganese(II) sulfate. They are black (**1**) or brown (**2**), lustrous, ribbon-like crystals which are air stable but rather difficult to handle because of spontaneous shrinking and twisting upon application of the slightest mechanical stress. Both compounds crystallize in the monoclinic space group $P2_1/c$ with four formula units in cells of dimensions $a = 11.575$ (2) Å, $b = 20.654$ (6) Å, $c = 7.323$ (1) Å, and $\beta = 103.73$ (1)° for **1** and $a = 11.692$ (2) Å, $b = 20.665$ (5) Å, $c = 7.360$ (2) Å, and $\beta = 103.84$ (2)° for **2**. Intensity data were collected on an automated Enraf-Nonius CAD-4 diffractometer with use of Mo Kα radiation. The collection of intensities of compound **1** could not be completed as the crystal suddenly "died out" without any premonitory anomalies in the standard intensities. The structures were solved from Patterson and Fourier analyses and were refined by full-matrix, least-squares techniques to R indices on F_o of 0.059 for the 120 variables and 894 reflections with $I > 1.5\sigma(I)$ for compound **1** and of 0.064 for the 155 variables and 1149 reflections with $I > 2\sigma(I)$ for compound **2**.[5]

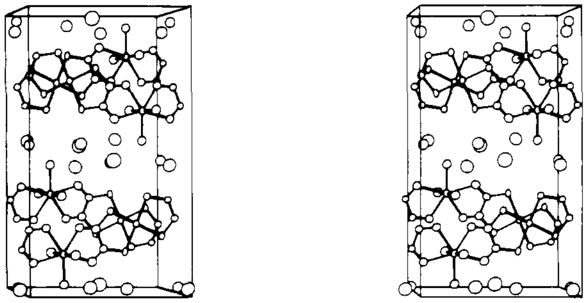


Figure 1. Stereoscopic view down the c axis (b axis vertical) of the unit cell of $Ni[Mn(H_2O)_3](S_2C_2O_2)_2{\cdot}4.5H_2O$, showing the sequence of alternating layers of water molecules (single circles) and of stacked bimetallic chains. For all atoms, 50% probability thermal ellipsoids or spheres are shown.

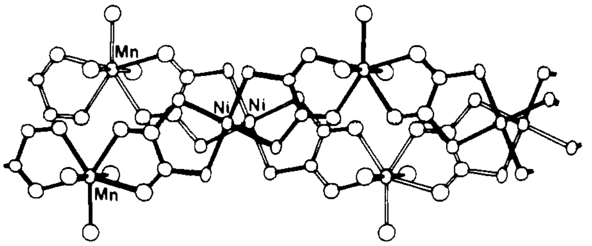


Figure 2. View of two successive chains of $\{Ni(S_2C_2O_2)[Mn(H_2O)_3](O_2C_2S_2)\}_\infty$ along a glide plane c represented by the dotted line.

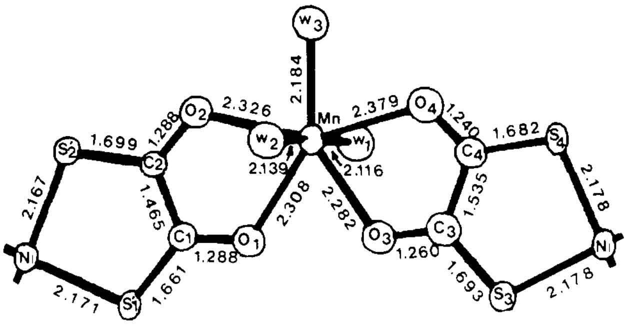


Figure 3. View of the chain repeat unit $Ni(S_2C_2O_2)[Mn(H_2O)_3](O_2C_2S_2)Ni$.

The two compounds are isostructural. Figures 1–3, illustrating their structures, are from the Ni derivative. The structures consist of "infinite"-chain molecules $\cdots A(S_2C_2O_2)[Mn(H_2O)_3](O_2C_2S_2)\cdots$ (A = Ni, Cu) criss-crossing glide planes c and stacked along these planes. Each layer of stacked chains is separated from the next one by intervening water molecules (Figure 1). Figure 2 illustrates the way two neighboring chains are related within a layer. A repeat unit $\{Ni(S_2C_2O_2)[Mn(H_2O)_3](O_2C_2S_2)\}$ is represented in Figure 3. The nickel (copper) atoms lie quite in the glide plane ($y = 0.2514$ (1) and 0.2518 (2), respectively); they are planarily coordinated to two dithiooxalate groups through their sulfur atoms. The Ni–S bond lengths (2.171 (5), 2.167 (5), 2.178 (5), 2.178 (5) Å) are about 0.1 Å shorter than the Cu–S ones (2.269 (6), 2.272 (7), 2.288 (6), 2.267 (6) Å). Angles around Ni and Cu are, respectively, S(1)–Ni–S(2) = 92.2 (2)°, S(1)–Ni–S(3) = 179.2 (6)°, S(1)–Ni–S(4) = 87.8 (2)°, S(2)–Ni–S(3) = 87.6 (2)°,

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[1] (a) Interrange, L. V. *ACS Symp. Ser.* **1974**, *No. 5.* (b) King, R. B. *Adv. Chem. Ser.* **1976**, *No. 150. Ibid.* **1979**, *No. 173.* (c) Kahn, O.; Charlot, M. F. *Nouv. J. Chim.* **1980**, *4*, 567–576. (d) Girerd, J. J.; Charlot, M. F.; Kahn, O. *Mol. Phys.* **1977**, *34*, 1063–1076 and references therein.

[2] Maury, F.; Gleizes, A.; Galy, J. *C. R. Hebd. Seances Acad. Sci., Ser. C* **1980**, *291*, 49–52.

[3] We have previously shown that the planar anion $Ni(S_2C_2O_2)_2^{2-}$ gives rise to one-dimensional stackings with alkali and alkaline earth ions as countercations: Gleizes, A.; Clery, F.; Bruniquel, M. F.; Cassoux, P. *Inorg. Chim. Acta* **1979**, *37*, 19–26. Maury, F.; Gleizes, A. *Ibid.* **1980**, *41*, 185–194. Gleizes, A.; Maury, F.; Cassoux, P.; Galy, J. *Z. Kristallogr.* **1981**, *155*, 293–305.

[4] We also synthesized palladium(II) manganese(II) and platinum(II) manganese(II) dithiooxalates. Their X-ray powder patterns look quite similar. The X-ray single-crystal structure of the Pt derivative was found to be identical with those of the Ni and Cu derivatives presented here.

[5] Listings of atomic positional and thermal parameters are available as supplementary material. See paragraph at the end of paper regarding supplementary material.

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