teriochlorin level does not significantly affect the core size. The values of C_t–N, C_t–C_m and C_t–C_α are similar in all four species ($\approx\pm0.01$ Å). The range of C_α–C_m distances (1.375–1.410 (7) Å) does differ from that found in ZnTPyP (1.402–1.413 (4) Å) and is indicative of the differences in π delocalization between the porphyrin and the hydroporphyrins (see Table III).

The Zn–N distances of 2.129 (4) and 2.115 (4) Å in rings I and III are longer than those of 2.036 (4) and 2.050 (4) Å in rings II and IV. Again, this elongation of the M–N (pyrrolines) is common to ZnTPC, ZnTPiBC, and several hydroporphyrins[18,19] and may reflect the wider C_α–N–C_α angles in rings I and III noted above. The M–N (pyrrole) distances are shorter than normally found in pentacoordinated Zn complexes;[18] the reason for the differences is not obvious.

The Zn is displaced 0.38 Å from the plane of the macrocycle toward the axial pyridine and 0.32 Å from the plane of the nitrogens, comparable to the deviations observed for ZnTPC, ZnTPiBC, and ZnTPyP. The Zn–N(py) linkage of 2.164 (5) Å is quite normal[18] and consistent with the values for the rest of the series. The pyridine is situated at 18.1° with respect to the N1–N3 direction and is tilted 6.5° from the normal to the plane of the macrocycle.

The macrocycle exhibits a slight saddle shape (Figure 3) with maximum deviations from the 24-atom plane of 0.22 Å at C2 and C13. Rings I–III are slightly twisted about the C_β–C_β bond with dihedral angles of 3.9, 3.4, and 7.6 (7)°, respectively, while the rotation around C17–C18 is 0.4 (7)°. Phenyl rings 1, 2, and 4 are nearly perpendicular to the macrocycle, but phenyl ring 3 lies at an angle of 69.3°, probably because of interactions with the solvent molecule, which is located 4.88 Å from its center (Figure 4).

Although the molecules pack in pairs, with Zn–Zn distances of 7.48 Å and C_t–C_t distances of 7.09 Å, they are well separated from each other, precluding strong π–π interactions. There are no contacts between adjacent molecules less than 3.9 Å, and the closest approach of ring centers is 4.37 Å between rings I and II in neighboring molecules.

As noted in the introduction, the electronic configurations of BChls are attracting intense theoretical interest because they control the photophysics and photochemistry of the chromophores and, consequently, the primary charge separation in photosynthesis.[3,13] The present results allow a calibration of the INDO/S method commonly used to treat BChls.[13] ZnTPBC offers the advantage of a high degree of symmetry without the complications, common to BChls, that arise from an additional exocyclic ring, orientations of substituents, and diverse deviations from planarity.[13] An INDO/S calculation was thus carried out for ZnTPBC·py, using the crystallographic coordinates reported here, with configuration interactions that included all single-excited configurations from the 10 highest occupied (HOMOs) into the 10 lowest unoccupied molecular orbitals (LUMOs). As expected from previous calculations,[20,21] the near degeneracy of the two HOMOs observed in porphyrins is removed and the HOMO is now a_{1u}, with the difference between the HOMO (a_{1u}) and the HOMO − 1 (a_{2u}) equal to 1.1 eV (for simplicity, the nomenclature associated with the D_{4h} symmetry of porphyrins is retained). EPR results for the cation radical of ZnTPBC that map the unpaired spin distribution of the HOMO support an a_{1u} orbital occupancy.[16] The loss of two double bonds, relative to porphyrins, destabilizes the π system of the bacteriochlorin, and the HOMO rises in energy, in agreement with experimental oxidation potentials: ZnTPBC is easier to oxidize than ZnTPP by $\approx$0.6 V.[16] In contrast to the behavior of the HOMO, the LUMO does not shift appreciably but the LUMO + 1 lies 1.58 eV above, thereby removing the degeneracy of the π^* orbitals found in porphyrins. Again, EPR results support this assignment; the anion radical of ZnTPBC yields well-resolved EPR spectra whereas those of $ZnTPP^{\bullet-}$ are unresolved because of Jahn–Teller effects associated with the degeneracy of the LUMOs.[22] Also, the experimental reduction potentials[16] of ZnTPBC and ZnTPP differ little (<0.1 V), indicating that the LUMOs in porphyrins and bacteriochlorins are nearly isoenergetic.

The invariance of the LUMO and the destabilization of the HOMO in bacteriochlorins result in a much smaller energy gap between the HOMO and LUMO and, consequently, in a significant red shift of the first absorption band of the chromophores relative to porphyrins. In solution, these transitions occur at 602 nm for ZnTPP·py[23] vs 752 nm (13 298 cm^{-1}) for ZnTPBC·py. The INDO calculations for the latter yield a value of 760 nm (13 160 cm^{-1}), a difference of only 8 nm or 140 cm^{-1}. Thus, the method does indeed correctly predict the Q_y optical transitions of bacteriochlorins. Not surprisingly, agreement with higher energy transitions is poorer (as much as 3000 cm^{-1} for the Soret bands), but the calculations clearly provide an adequate electronic description of the chromophores, particularly for the frontier orbitals that are crucial for photochemical activity in photosynthetic electron transfer and photodynamic therapy.

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Supplementary Material Available: Tables giving complete crystal data, selected bond angles, fractional coordinates for the hydrogen atoms of ZnTPBC, and final positional and anisotropic thermal parameters for the non-hydrogen atoms of ZnTPBC (6 pages); a table of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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(20) Gouterman, M. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1978; Vol. III, p 1.

(21) Chang, C. K.; Hanson, L. K.; Richardson, P. F.; Young, R.; Fajer, J. *Proc. Natl. Acad. Sci. U.S.A.* **1981**, *78*, 2652.

(22) Fajer, J.; Davis, M. S. In *The Porphyrins*; Dolphin, D., Ed.; Academic Press: New York, 1979; Vol. IV, p 197.

(23) Nappa, M.; Valentine, J. S. *J. Am. Chem. Soc.* **1978**, *100*, 5074.

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Vapor Pressure of Pentacarbonylruthenium, $Ru(CO)_5$

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Ruthenium carbonyls play an important role in different catalytic processes with carbon monoxide, e.g., the carbonylation of olefins,[1] the formation of ethylene glycol,[2] the synthesis and homologation of alcohols,[3] and the water gas-shift reaction.[4] The most convenient catalytic precursors for these and other reactions are $Ru_3(CO)_{12}$ and $Ru_4H_4(CO)_{12}$. However, the monomer $Ru(CO)_5$ is readily formed therefrom under reaction conditions upon addition of CO.[5] Despite its importance, the vapor pressure of pentacarbonylruthenium has not been reported until now.

For the investigation of the ruthenium-catalyzed carbonylation of olefins, the thermal carbonylruthenium equilibria between $Ru_3(CO)_{12}$, $Ru(CO)_5$, and CO[6] as well as $Ru_4H_4(CO)_{12}$, $Ru_3(CO)_{12}$, $Ru(CO)_5$, CO, and H_2[6,7] were quantitatively studied in *n*-hexane under elevated temperature and pressure.[5] Therefore, for precise treatment of the data, it is necessary to know the vapor pressure of $Ru(CO)_5$.

$Ru(CO)_5$ is, at room temperature, a colorless liquid that decomposes under light easily to $Ru_3(CO)_{12}$, unless stabilized with CO.[8] To avoid any photochemical reaction, the vapor pressure of $Ru(CO)_5$ has to be determined under the total exclusion of light. At elevated temperature the presence of CO is needed to avoid

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Table I. Experimental Data for the Vapor Pressure of $Ru(CO)_5$[a]

T, °C	*P*, mbar	*T*, °C	*P*, mbar
-15.0[b]	10	-15.0	10
-10.2	14	-15.0	10
-4.8	20	-12.5	12
-3.6	24	-10.2	16
0.0	32	-10.0	16
4.8	41	-5.0	21
12.0	63	-5.0	23
19.3	112	-0.2	31
29.5	151	5.0	44
		10.0	58
-15.1[c]	10	10.0	61
-10.0	15	15.0	80
-7.5	19	19.6	104
0.0	31	22.8	124
		33.0	210
-30.0[c,d]	3	38.2	270
-22.5[d]	5	50.0	439
-20.0	6	9.8[e]	79
-17.5	7		

[a] ±1 mbar. [b] Measured without added CO. [c] Different experiments with approximately 1 bar of CO (at 0 °C); if the volume and the number of moles of CO remain constant, the ratio $p\{CO\}/T$, determined at low temperatures with $p\{Ru(CO)_5\} \sim 0$, is constant as well. This can be subtracted from the equation $p\{tot\}/T = p\{CO\}/T + p\{Ru(CO)_5\}/T$ and leads to the vapor pressure of the pentacarbonyl. It can be seen in Figure 1 that no systematic error was made. [d] The melting point of $Ru(CO)_5$ is reported as -22 °C.[8] The vapor pressures below this temperature are due to sublimation rather than evaporation. [e] Measured after the 50.0 °C data point; contains CO due to decomposition to $Ru_3(CO)_{12}$.

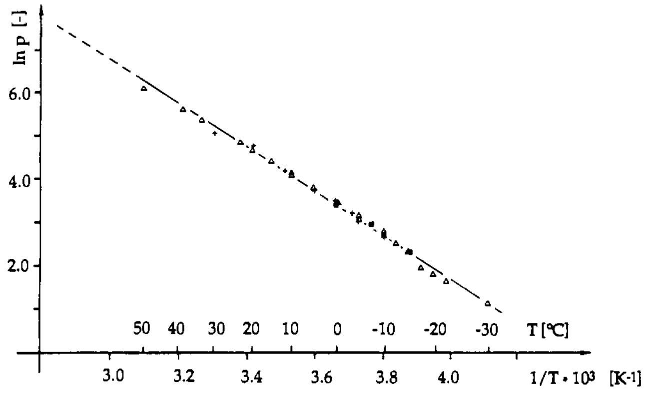

Figure 1. ln $p\{Ru(CO)_5\}$ vs $1/T$ diagram of the vapor pressure data, measured without (+) and with (■, △) approximately 1 bar of CO. (See footnote *b* of Table I.)

thermal decomposition to $Ru_3(CO)_{12}$ and CO. Therefore, the vapor pressure of pentacarbonylruthenium, $Ru(CO)_5$, was measured in a stainless steel autoclave between -30 and +50 °C (for the data, see Table I) both without and with approximately 1 bar of CO (see Table I). A plot of ln $p\{Ru(CO)_5\}$ vs $1/T$ leads to eq 1 (p in mbar, T in K). Therefrom, the enthalpy of evaporation

$$\ln p\{Ru(CO)_5\} = -5072/T + 21.95 \qquad (1)$$

ΔH°_{vap} for $Ru(CO)_5$ can be calculated as 42.2 ± 0.6 kJ/mol, and at 64 ± 6 °C, the vapor pressure is 1.0 bar (if $Ru(CO)_5$ is stabilized with CO) (Figure 1).

The accuracy of the apparatus was checked by measuring first the vapor pressure of toluene. Its enthalpy of evaporation was found to be 35 690 J/mol, and its boiling point, 110.4 °C. Both, ΔH°_{vap} and T_{bp}, are within experimental errors compared with the reported values of 35 901 and 39 198 J/mol, respectively, and 110.6 °C.[9]

The enthalpy of evaporation of $Ru(CO)_5$ is slightly higher than that reported for $Fe(CO)_5$ with 40.2[10] and 40.1 kJ/mol,[11] respectively. This trend is observed also with the hexacarbonyls of the triad Cr-Mo-W. The enthalpy of sublimation ΔH_{subl} rises from $Cr(CO)_6$ (71.6,[12] 71.4 kJ/mol[13]) to $Mo(CO)_6$ (76.9,[12] 73.8 kJ/mol[13]) and $W(CO)_6$ (78.9,[12] 76.4 kJ/mol[13]). In contrast to this behavior, a different trend for the boiling points was observed. This was found to be lower for the carbonyls of the 4d metals as compared to the 3d ones in both the present work (bp$\{Ru(CO)_5\}$ = 64 °C vs bp$\{Fe(CO)_5\}$ = 104.7[14] and 100.3 °C,[11] respectively) and the one reported for the Cr triad (bp$\{Mo(CO)_6\}$ = 138 °C vs bp$\{Cr(CO)_6\}$ = 143 °C and bp$\{W(CO)_6\}$ = 257 °C).[12] The reason for this is unclear and may come from different intermolecular forces.

Experimental Section

A 500-mL stainless steel autoclave was charged with 0.7938 g (=1.242 mmol) of $Ru_3(CO)_{12}$ (prepared according to the method of Johnson and Lewis[15]) and 160 bar of CO and heated to 160 °C.[16] After 48 h the autoclave was cooled slowly to -78 °C and the carbon monoxide released. The autoclave was then warmed to room temperature and connected with a 100-mL autoclave (fitted with a piezoresistive pressure transducer, -1.0 to +1.5 bar), which was cooled to -78 °C. Both autoclaves were evacuated with a high-vacuum pump. Thereafter, $Ru(CO)_5$ was evaporated in the first (500 mL) autoclave and trapped in the second (100 mL). Therein, the vapor pressure measurements (±0.001 bar) were carried out. The autoclave was thermostated until the pressure remained constant for at least 10 min (thermostating for a longer period showed no pressure changes) within an accuracy of ±0.1 °C. The infrared spectrum of a sample of the measured ruthenium carbonyl was recorded, and the unambiguous two bands for $Ru(CO)_5$ (2037 cm^{-1}, ϵ = 6570 ± 40 dm^3/(mol cm) and 2002 cm^{-1}, ϵ = 8100 ± 50 dm^3/(mol cm); in *n*-hexane) were observed.

Registry No. $Ru(CO)_5$, 16406-48-7.

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(1) Knifton, J. F. *J. Mol. Catal.* **1988**, *47*, 99 and references therein. Cooper, J. L. U.S. Pat. 4602116, 1986.

(2) E.g. Agency of Industrial Sciences and Technology; JP 58172334 (1982), JP 59190938 (1984), JP 60199842 (1984).

(3) E.g. Agency of Industrial Sciences and Technology; JP 58172332 (1982), JP 59190937 (1983).

(4) Darensbourg, D. J.; Ovalles, C.; Pala, M. *J. Am. Chem. Soc.* **1983**, *105*, 5937.

(5) Koelliker, R. ETH Dissertation No. 8704, 1988.

(6) Piacenti, F.; Bianchi, M.; Frediani, P.; Benedetti, E. *Inorg. Chem.* **1971**, *10*, 2759.

(7) Rossetti, R.; Stanghellini, P. L. *Inorg. Chim. Acta* **1983**, *70*, 121.

(8) Bruce, M. I. *Comprehensive Organometallic Chemistry*; Pergamon Press: Oxford, England, 1982; Vol. 4, p 662.

(9) *Handbook of Chemistry and Physics*, 64th ed.; CRC Press: Boca Raton, FL, 1983-84; C-541, C-692.

(10) Cox, J. D.; Pilcher, G. *Thermochemistry of Organic and Organometallic Compounds*; Academic Press: London, 1970; p 493.

(11) Gilbert, A. G.; Sulzmann, K. G. P. *J. Electrochem. Soc.* **1974**, *121*, 832.

(12) Boxhoorn, G.; Ernsting, J. M.; Stufkens, D. J.; Oskam, A. *Thermochim. Acta* **1980**, *42*, 315.

(13) Skinner, H. A., Ed. *Phys. Chem. Ser. 2* **1975**, *10*, 64.

(14) *Gmelin Handbuch der Anorganischen Chemie*; Springer Verlag: Berlin, 1979; Eisen-Organische Verbindungen Teil B3, p 23.

(15) Johnson, B. F. G.; Lewis, J. *Inorg. Synth.* **1972**, *13*, 92.

(16) Rushman, P.; van Burren, G. N.; Shirallan, M.; Pomeroy, R. K. *Organometallics* **1983**, *2*, 693.

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Reaction of Hydride with $(\eta^5\text{-}C_9H_7)Re(CO)_3$. Facile Formation of $[H_6Re_4(CO)_{12}{}^{2-}]$ and Indenide

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η^5-Cyclopentadienyl and η^5-indenyl ring slippage has been postulated as a prerequisite for substrate activation in certain catalytic processes.[1] Consistent with this notion are the rapid