This possibility was investigated as follows: assuming easily-derived relationships among *a*, *b*, *c* and *d*, a computer program was developed which minimized the deviations of the experimentally-determined values of k_{obsd} from a line determined by eqn (10) as the values of *a*, *b*, *c* and *d* were varied within the constraints imposed by the relationships.† It was found that very reasonable values of the coefficients could be obtained such that the standard deviations of points from the curves described by (10) were comparable to the standard deviations of the points from the best least-squares line obeying eqn (6). Typical plots of k_{obsd} vs $[PBu_3^n]$ obtained through use of this program are exhibited in Fig. 2.

Thus it is demonstrated that the data are best rationalized in terms of mechanism (7), for which rate law (8) is applicable. Given the complexity of this rate law, however, no significance should be attached to actual values of the coefficients obtained through the data analysis.

However, the results clearly demonstrate the accessibility of two reaction pathways in this system, one involving unimolecular ring-opening, the second, a concerted displacement of one end of the chelating ligand by PBu_3^n. Thus (1) obeys the generalization that two reaction pathways are observed in the great majority of ligand-exchange reactions of the octahedral carbonyl complexes of Cr, Mo and W[2]. That two such pathways are observed for the three metals, for substrates containing a wide range of substituents, and for an equally wide range of incoming nucleophiles, indicates that the two pathways are closely-related, and thus that the interchange process most probably involves significant bond-breaking accompanying formation of the transition state.

Acknowledgements—The support of this research by the Robert A. Welch foundation under Grant #B-434 and by the North Texas State University Faculty Research Fund is gratefully acknowledged.

Department of Chemistry
North Texas State University
Denton, TX 76203
U.S.A.

GERARD R. DOBSON*
LINDA D. SCHULTZ‡
BERNARD E. JONES
MARTIN SCHWARTZ

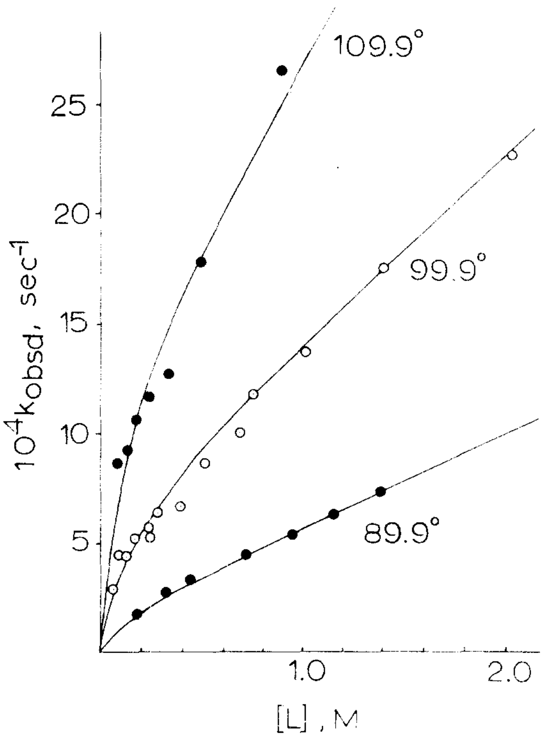

Fig. 2. Plots of k_{obsd} vs $[PBu_3^n]$ for reaction of $(DTO)W(CO)_4$ with PBu_3^n at three temperatures. curves are computer-drawn, assuming rate law (10).

REFERENCES

1. Part LXV: G. R. Dobson and A. Moradi-Araghi, *Inorg. Chim. Acta.* in press.
2. For a recent review, see, G. R. Dobson, *Acc. Chem. Res.* **8**, 300 (1976).
3. L. D. Schultz and G. R. Dobson, *J. Organometal. Chem.* **124**, 19 (1977).
4. G. R. Dobson and L. D. Schultz, *J. Organometal. Chem.* **131**, 285 (1977).
5. G. R. Dobson and Honors Science 102-2, *J. Coord. Chem.* **7**, 253 (1978).
6. See, e.g. J. R. Graham and R. J. Angelici, *Inorg. Chem.* **6**, 2082 (1967); J. R. Graham and R. J. Angelici, *Inorg. Chem.* **6**, 992 (1967).
7. S. O. Grim and D. A. Wheatland, *Inorg. Chem.* **8**, 1716 (1969).
8. See, Ref. [3], footnote 27.

---

*Author for correspondences.

†The following conditions were imposed: (a) The constraints imposed by the limiting values of *a*/*c* and *b*/*d* obtained from plots of $k_{obsd}/[PBu_3^n]$ vs $[Bu_3^n]$ were observed; (b) Values of *a* and *b*. and *c* and *d* such that limiting rate behavior was not observed were chosen; (c) Reasonable variations of *a*/*b* and *c*/*d* as a function of temperature were required.

‡Present address: Department of Chemistry, Tarleton State University, Stephenville, TX 76402, U.S.A.

J. inorg. nucl. Chem. Vol. 41, pp. 121–122

0022-1902/79/0101-0121/$02.00/0

On the purported $[Coen_2S_2O_3Cl]$ and $[Coen_2S_2O_3]Br$

(*First received* 30 *January* 1978; *in revised form* 19 *May* 1978)

In the cousse of trying to prepare thiosulfate complexes of Co(III), we found two reported preparations, for $[Coen_2S_2O_3Cl]$ [1] and for $[Coen_2S_2O_3]Br$ [2], that appear to be in error. The purpose of this note is to correct these reports.

EXPERIMENTAL

Reagent grade chemicals were used throughout. Chromatographic separations were performed on Sephadex SP-C25-120 and Q-25-120, cation and anion exchange resins, respectively, eluting with dilute NaCl or $NaClO_4$ solutions at neutral pH. Visible-UV spectra were taken on a Beckman DB-GT and IR spectra were obtained on a Perkin-Elmer 337 in Nujol mulls between KBr plates.

RESULTS AND DISCUSSION

$[Coen_2S_2O_3Cl]$. Sen Gupta (1) reported that the action of thiosulfate on an aqueous solution of *trans* $[Coen_2Cl_2]Cl$ or *trans* $[Copn_2Cl_2]Cl$ resulted in the precipitation of dark-green, crystalline solids, which he identified as $[Coen_2ClS_2O_3]$ and $[Copn_2ClS_2O_2]$, respectively, on the basis of elemental analyses. Repeating his preparations for both the ethylenediamine (*en*) and propylenediamine (*pn*) homologues, we confirm the production of sparingly soluble dark-green crystalline solids; for simplicity we refer to the *en* homologue hereafter, although similar results were obtained for the *pn* compounds. Chromatographic separation of an aqueous solution of the dark-green solid produces no evidence of a charge-neutral species; rather two ions are found, the UV-vis spectra and chromatographic behavior of which match that of the cation, *trans* $[Coen_2Cl_2]^+$ (λ_{max}(nm): 616, 436 (sh), 390, 304, 248), and the anion, *trans* $[Coen_2(S_2O_3)_2]^-$ (λ_{max}(nm): 596 (sh), 544, 334, 213), to which Akamatsu *et al.* [3] have assigned a bis (aniono-S) structure on the basis of this spectrum. The IR spectrum of the solid (1360–450 cm^{-1}) contains no lines not contained in the spectra either of *trans* $[Coen_2Cl_2]Cl$ or of Na *trans* $[Coen_2(S_2O_3)_2]$ [4]. Moreover a saturated solution of Na *trans* $[Coen_2(S_2O_3)_2]$ mixed with a saturated solution of *trans* $[Coen_2Cl_2]Cl$ produces a dark-green, crystalline solid whose spectral properties match that of the compound discussed above. We conclude that there is no evidence to support the structural assignment of $Coen_2S_2O_3Cl$ (or $Copn_2S_2O_3Cl$); rather the appropriate formulation is the monocationic-monoanionic salt, *trans* $[Coen_2Cl_2]^+$ *trans* $[Coen_2(S_2O_3)_2]^-$, and similarly for the *pn* homologue.

$[Coen_2S_2O_3]Br$. Duff's preparation [2a] of this salt from $[Coen_2O_2CO]Br$ and $BaS_2O_3{\cdot}H_2O$ was verified by Ray and Sarkar[5] and promulgated in Schlessinger's preparative handbook [2b], in which a quantitative yield was reported. In our hands, repeated attempts to prepare $[Coen_2S_2O_3]Br$ yield a brown solid of variable composition; chromatographic separation of a solution of the crude product reveals the presence of at least four anions and three cations. The UV-visible spectra and chromatographic behavior are consistent with the principal cation being $[Coen_3]^{3+}$, with trace amounts of $[Coen_2(OH_2)(SO_3)]^+$ [6] and unreacted $[Coen_2O_2CO]^+$; the principal anions are *cis* and *trans* $[Coen_2(S_2O_3)_2]^-$ [3] and Br^-; recrystallization from water yields a solid of variable composition containing only $[Coen_3]^{3+}$, Br^- and *trans* $[Coen_2(S_2O_3)_2]^-$. No evidence of an unidentified univalent cation in other than trace amounts is found. We conclude there is no evidence for the production of the salt $[Coen_2S_2O_3]Br$.

Chemistry Department,
Bucknell University,
Lewisburg, PA 17837
U.S.A.

J. A. SHAMAY
J. N. COOPER*
R. J. BARTO

---

*Author for correspondence.

REFERENCES

1. N. Sen Gupta, *Z. Anorg. Allg. Chem.* **326**, 108 (1963).
2. (a) J. Duff, *J. Chem. Soc.* 450 (1922). (b) G. Schlessinger, *Inorganic Laboratory Preparations*, p. 249. Chemical Publishing, New York (1962).
3. K. Akamatsu, J. Hidaka and Y. Shimura, *Bull. Chem. Soc. Japan* **50**, 533 (1977).
4. A. Babaeva, I. Baranovskii and Yu. Kharitonov, *Russ. J. Inorg. Chem.* **8**, 307 (1963).
5. B. Ray and P. Sarkar, *J. Ind. Chem. Soc.* **10**, 625 (1933).
6. M. Baldwin, *J. Chem. Soc.* 3125 (1961).

J. inorg. nucl. Chem. Vol. 41, pp. 122–124
© Pergamon Press Ltd., 1979. Printed in Great Britain
0022-1902/79/0101-0122/$02.00/0

Reactions of copper(II) complexes of phenylamido substituted quadridentate Schiff-base ligands

(*Received* 6 *April* 1978)

The quasi-aromatic property of the coordinated β-diketones has been substantiated by their facile electrophilic substitution reactions at the ring γ-CH carbon[1]. Attempts have been made to isolate the complexes with hetero groups at the ring γ-CH carbon to understand the influence of a substituent on the quasi-aromatic property of the other chelate ring(s). Complexes of this type have been isolated in the case of tris(acetylacetonato)cobalt(III)[2]. However, similar complexes are not known in the case of β-ketoimine complexes. In fact, the reactions of β-ketoimines are much less investigated[3], probably due to their hydrolytic instability. This note reports reactions of Schiff-base Cu(II) complexes (1a and 1b, Scheme 1) with N-bromosuccinimide, N-chlorosuccinimide, N_2O_4 and nitric oxide and characterization of the resulting products.

EXPERIMENTAL

Materials. The mono-substituted phenylamido Schiff-base copper(II) complexes (1a and 1b) were prepared by reacting ammoniacal copper(II) solution in methanol with N,N′-ethylene/iso-propylene-bis(acetylacetoneimine) and phenylisocyanate (mole ratio 1 : 1) in ether. Pale violet crystals of the complex were obtained after keeping the reaction mixture at room temperature for 2 hr. The yields of the complexes (95%) obtained by this procedure are much higher than that by the reported method[4]. N-bromosuccinimide (NBS), N-chlorosuccinimide (NCS) (both Riedel) were recrystallized from water before use. Nitric oxide[5] and N_2O_4[6] were prepared by the known procedures. Analar grade solvents were used for the preparation and purification of the complexes.

Preparation of the complexes. Reaction of 1a (i) with NBS or bromine vapours: A mixture of 1a (0.001 mole) and N-bromosuccinimide (0.001 mole) in 50 ml chloroform was refluxed over a waterbath for about 7 hr. The solution was cooled and ether (100 ml) was added to obtain a green precipitate (50%). It was filtered, washed thoroughly with ether and recrystallised from chloroform. Reaction of the complex with bromine vapours offered the same complex. (ii) with NCS: A procedure analogous to the one described in (i) was employed in the reaction of 1a with NCS. The complex was recrystallised from chloroform. Yield, 55%. (iii) With N_2O_4: A clear solution of 1a (0.001 mole) in chloroform was treated with N_2O_4. The reaction mixture was maintained at room temperature for about 4–6 hr. Addition of ether (100 ml) to the resulting dark reddish solution yielded a brown precipitate. It was filtered and recrystallised from chloroform. Yield, 70%. (iv) With nitric oxide. The complex 1a (0.002 mole) was dissolved in chloroform (80 ml). Nitric oxide purified over sodium hydroxide pellets was then bubbled vigorously through the above solution for about an hour, during which the colour of the solution changed from violet to dark brown. The reaction vessel was closed and left at room temperature for