Identification of New Species by Magnetic Circular Dichroism: Square-planar S_4^{2+}

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Summary Identification of the new species, square-planar S_4^{2+}, by magnetic circular dichroism is reported.

GILLESPIE AND HIS CO-WORKERS have recently identified square-planar Se_4^{2+} and Te_4^{2+} ions in solutions of selenium and tellurium in oxidising solvents such as oleum and HSO_3F–$S_2O_6F_2$.[1–5] We report here the magnetic circular dichroism (m.c.d.) of solutions of sulphur, selenium, and tellurium in sulphuric acids. The data indicate the existence of the S_4^{2+} homologue.

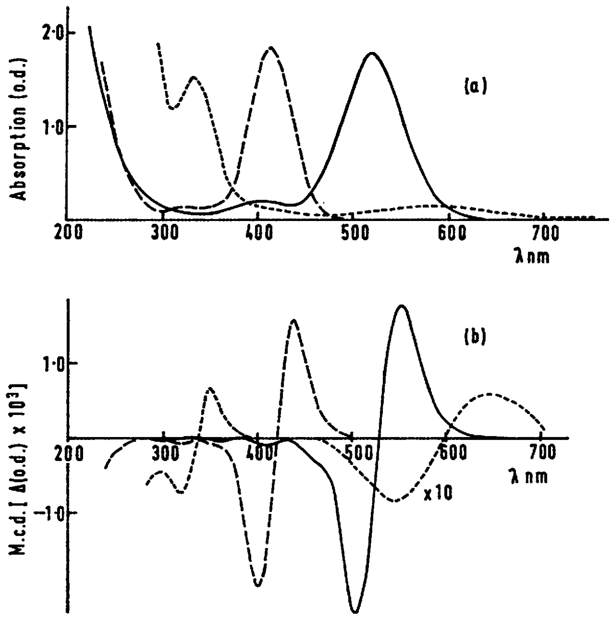

FIGURE. *Absorption spectra,* (a) *and m.c.d.,* (b), *of:*

Te–*conc. sulphuric acid* (<3·8 *g./ litre,* 1 *mm. pathlength,* 2½ *days old*) (————).

Se–$(NH_4)_2S_2O_8$–30% *fuming sulphuric acid* (0·980 *and* 14·880 *g./litre,* 1 *mm. pathlength,* 12 *hr. old*) (— — — —).

S–30% *fuming sulphuric acid* (0·011 *g./litre,* 1 *cm. pathlength,* 4 *weeks old*) (- - - - - -).

Δ(o.d.) = $(o.d.)_L - (o.d.)_R$. *M.c.d. data refer to* 49·5 *k*G *in the direction of the light beam.*

The absorption spectra of solutions of Se in 30% fuming sulphuric acid containing $(NH_4)_2S_2O_8$ and of Te in concentrated sulphuric acid are shown in the Figure, (a). Each spectrum contains one strong band in the visible—near u.v. region, identified by Gillespie *et al.* with Se_4^{2+} and Te_4^{2+} respectively.[1,2]† The 410 nm Se_4^{2+} band was assigned by Brown *et al.*[4] to a transition between π-orbitals of the square-planar ring deriving from Se $4p$-orbitals.

The associated m.c.d.‡ is presented in the Figure, (b). The 410 nm Se_4^{2+} and 510 nm Te_4^{2+} bands show similar S-shaped m.c.d., identical in sign and with comparable $[\Delta(o.d.)]_{max}$: $[o.d.]_{max}$ ratios. As is discussed fully elsewhere,[6] these results point to highly symmetrical absorbing species (given their diamagnetism[1,2]), and hence support the assignment of square-planar structures to Se_4^{2+} and Te_4^{2+}. Accepting this geometry, the m.c.d. further indicates the strong bands to arise from in-plane polarized transitions, which is consistent with the π-electron model.

Solutions of sulphur in fuming sulphuric acid exhibit two distinct absorption bands at 330 and 590 nm, the latter producing the characteristic blue colour.[7]§ In addition, two radicals have been observed by e.s.r.,[8,9] one (R^1) being present in all solutions, the other (R^2) occurring only at lower SO_3 concentrations. These species have not been conclusively identified, although various assignments have been suggested.[8,9] Since R^1 and the blue colour always occur together (and also in solutions in SbF_5)[9] it appears that R^1 is responsible for the 590 nm absorption band.

The absorption and m.c.d. spectra of a solution of S in 30% fuming sulphuric acid are shown in the Figure, (a) and (b). The m.c.d. of the 330 nm band is identical in form and sign and of similar magnitude to that of the strong bands of Se_4^{2+} and Te_4^{2+}. We therefore infer that the 330 nm band belongs to square-planar S_4^{2+} and is the analogue of the 410 nm and 510 nm bands of Se_4^{2+} and Te_4^{2+}. The m.c.d. also changes sign through the blue band; this is not

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† Owing to the probable existence of other species in our solutions exact extinction coefficients cannot be evaluated. Lower limits can be calculated, however: for Se_4^{2+} and Te_4^{2+} we obtain 5900 and 5000 respectively.

‡ The m.c.d. measurements were made in the laboratory of Professor C. Djerassi at Stanford University, under the direction of Dr. E. Bunnenberg and with the assistance of Mrs. R. Records. We thank them for their generous assistance.

§ Lower limits for ϵ_{max} per mole of S atoms are 50 and 475 for the 590 and 330 nm bands respectively.

inconsistent with previous assignments of R[1]. Without firmer identification, however, further discussion of the m.c.d. is not profitable.

In view of the tendency of sulphur to ring formation, an S_4^{2+} ring is not surprising. With this assignment the strong bands of S_4^{2+}, Se_4^{2+}, and Te_4^{2+} form a sequence, decreasing monotonically in energy from S to Te. That the transition in S_4^{2+} is comparable in energy to the $\pi \rightarrow \pi^*$ transition of S_2[10] adds support to the π-electron model for these transitions.

We believe this to be the first instance in which a new molecular species has been *initially* identified by magnetic circular dichroism. In the realm of small inorganic species m.c.d. would appear to have considerable future application.

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