Available online at www.sciencedirect.com
ScienceDirect
Mendeleev Commun., 1994, 4(1), 5–7
Mendeleev Communications

Reactions of Samarium Atoms in Inert and Reactive Matrices

Werner E. Klotzbücher,*[a] Marina A. Petrukhina[b] and Gleb B. Sergeev[b]

[a] Max-Planck-Institut für Strahlenchemie, Postfach 10 13 65, D–45413 Mülheim an der Ruhr, Germany. Fax: +49 208 304 3951

[b] Department of Chemistry, M. V. Lomonosov Moscow State University, 119889 Moscow, Russian Federation. Fax: +7 095 939 0126

Cocondensation of samarium vapour with inert gases at cryogenic temperatures yields isolated samarium atoms and small clusters, while in complementary depositions with CO and N_2 novel carbonyl and dinitrogen complexes are formed. Surprisingly, 'naked' samarium atoms can be observed at 9 K in pure dinitrogen.

Research on the properties of mono- and bimetallic small metal clusters is of practical interest for the development of novel metal catalysts. In the past these studies focused on the alkali, d-shell transition and noble metal clusters, demonstrating that the properties of most clusters change drastically on going from dimers and trimers to small cluster units exhibiting some characteristics of bulk metal. Lately the coordination and organometallic chemistry of the lanthanide metals, characterized by their partially filled 4f-subshells, has gained interest due to their peculiar magnetic, superconducting and catalytic properties.[1–4] Thus, *e.g.* Sergeev *et al.*[5] and Imamura *et al.*[6] have shown that cocondensation of the elements with organic media yields low-valent, highly dispersed organometallic particles which exhibit unusual activity and selectivity for hydrogenation and isomerization processes, and Klabunde[7] lists a number of promising complexes generated by metal vapour cocondensation.

Some ten years ago one of us[8] investigated the optical properties of nearly all isolated d-block metal atoms and clusters, as well as their behaviour upon irradiation ('photo-aggregation'), by trapping the species in rare gas matrices at cryogenic temperatures. Further studies included the synthesis of 'naked' bimetallic dimers and trimers and of novel carbonyl and dinitrogen species of these metals.[9–11] As very little is known about the properties of the related lanthanide systems, we have started a systematic investigation of the cocondensation and photochemical reactions of lanthanide atoms in inert and reactive cryogenic matrices, using techniques and experimental conditions described previously,[9,10] with the aim of identifying small clusters and binary metal ligand complexes. In this communication we present our preliminary data on the samarium system.

The optical spectra resulting from cocondensation of samarium vapour with a great excess ($1:10^5$) of argon or methane at 9 K (full cooling power) are displayed in Fig. 1. The positions are listed (in cm^{-1} energy units for comparison of shifts) in Table 1 together with our data for krypton matrices.[12] Particularly in the methane marix the band positions of the narrow absorptions correlate very well with the respective gas-phase data[13] (stick spectrum) exhibiting only minimal band splitting (partially removed upon annealing) and hardly any shift.

The optical spectrum of samarium atoms in an argon matrix shows more severe splitting. As the electronic transitions of gas-phase samarium are energetically well spaced, and the

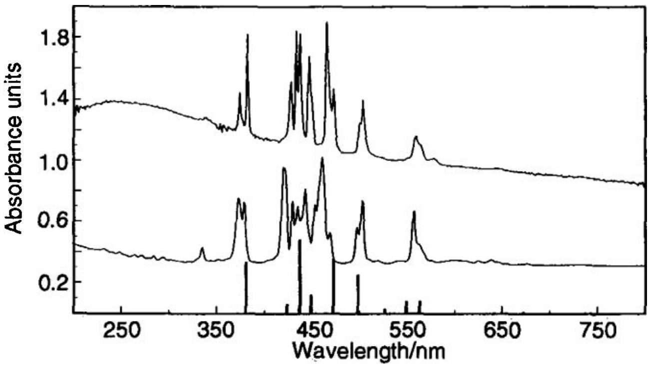

Fig. 1 UV–VIS spectra of samarium atoms isolated at 9 K in an argon (lower trace) and a methane matrix (upper trace). The corresponding gas phase data[13] are indicated as a stick spectrum.

absorptions in the cryogenic matrices exhibit half-width of 50–80 cm^{-1}, reliable assignments are still possible. These indicate blue shifts of up to 800 cm^{-1}. (By contrast the spectra obtained for second- and third-row d-block transition metals [11] generally exhibit blue shifts of 1000 cm^{-1}, and occasionally far more). Upon annealing to 25 K only a few band shoulders vanish, indicating that most band splittings are caused by direct interaction of the $4f^66s^2$ orbitals with the matrix cage: either there exist several stable matrix sites or formally forbidden transitions are becoming allowed in the cage crystal fields.

Increasing the metal sublimation rate, keeping all other conditions constant, results in a less intense optical spectrum of samarium atoms, but with additional features growing in at 727, 599(s), 541 and 352 nm in solid argon. By comparison with previous studies of transition metals these bands can be associated with the onset of nucleation, most probably the formation of the samarium dimer, Sm_2.

An alternative route to the formation of small clusters is cocondensation at slow metal sublimation rates without applying full cooling power. Even at deposition temperatures of 10 K the 599 nm band, the most intense feature of the dimer pattern, has already grown discernibly, and in 15 K depositions its intensity is comparable to those of the atomic absorptions. Above *ca.* 13 K deposition temperature a second set of absorptions grows in at 518, 470 and 390/400 nm, indicating the formation of trimers or higher clusters. Depositions above 15 K yield only a steeply rising background with weak remnants of atomic absorptions.

A third route to cluster formation is photoexcitation of the metal atom by narrow-band irradiation into any major resonance absorption, which for some d-block metals[8,11] was shown to result in 'photomobilization' with subsequent metal aggregation. In the case of samarium in argon brief irradiations result in removal of some matrix splittings of the metal atom absorptions, and, if present, immediate loss of all cluster features. Prolonged irradiations (15–100 min) result in more than 50% loss of the atomic features, accompanied by band broadening, and growth of a new absorption at 646 nm, probably associated with a samarium cluster or particle of unknown composition.

Metal carbonyl and metal dinitrogen complexes of samarium are not known (only metal carbonyl derivatives of samarium have been reported by Beletskaya *et al.*[14]), and thus it is of great interest to investigate the direct reaction of samarium atoms with these prospective ligands. The optical and vibrational spectra obtained after cocondensation of samarium atoms with pure carbon monoxide at 9 K are displayed in Fig. 2(*a*). Only weak traces of the atomic absorptions of samarium can be observed in the UV-VIS spectrum, on top of a broad band centred at 402 nm. The first impression, that essentially all atoms have combined with CO, is strengthened by the observation of only one strong absorption in the carbonyl vibrational stretching region at 1987 cm^{-1}, with a shoulder at 1959 cm^{-1}.

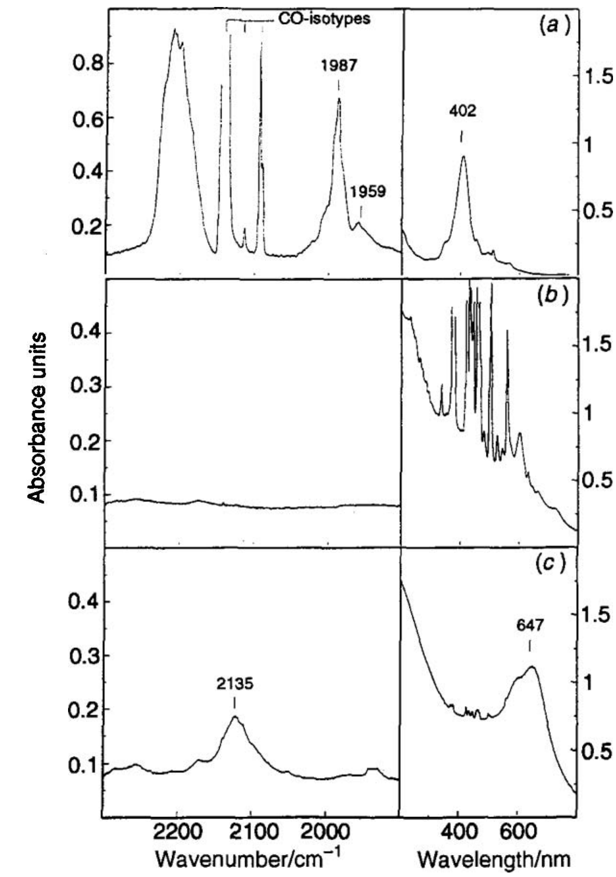

Fig. 2 IR and UV–VIS spectra obtained after cocondensation at 9 K of samarium atoms with (*a*) pure carbon monoxide, (*b*) pure dinitrogen, indicating the presence of 'naked' samarium atoms in the reactive matrix and (*c*) pure dinitrogen, followed by 60 s irradiation at 502 nm, demonstrating complete conversion to the $Sm(N_2)_6$ species.

A few seconds of irradiation into an atomic absorption is sufficient to have the remaining atoms react, which can be monitored by an increase in the IR absorption band. Under matrix experimental conditions the new complex, by design a binary metal carbonyl, is stable upon irradiation at 400 nm, and thermally stable upon annealing up to 30 K and recooling. We therefore conclude that the highest coordination complex has been formed already on deposition. Lanthanides are known to exhibit an extraordinary manifold of coordination numbers, ranging up to 12. However, the vibrational and electronic absorptions of the new species resemble strongly those observed for the known $Ti(CO)_6$, $V(CO)_6$ and $Cr(CO)_6$ complexes. Clarification is achieved by codeposition of samarium atoms with a 7:1 mixture of ^{12}CO and ^{13}CO, which yields a single further line at 1955 cm^{-1}, the correct position for a mono-substituted hexacarbonyl metal complex. The proposed $Sm(CO)_6$ complex is formally a 14- to 20-electron species, depending on the degree of f-orbital involvement.

While transition metal carbonyls are well-known stable species, the isoelectronic and isostructural dinitrogen complexes are rare and labile, with most of them synthesized under low-temperature matrix conditions. The IR and UV-VIS spectra obtained after deposition of samarium with pure dinitrogen at 9 K are displayed in Fig. 2(*b*). They show that the highly reactive 'naked' atoms have *not* reacted with the prospective ligand. Band positions and shifts are similar to the data observed for samarium atoms in a methane matrix (Table 1); even the strong band of uncomplexed Sm_2 can be observed at 600 nm. However, subsequent 502 nm irradiation yields, within 1 min, a gradual and complete reaction to a new species characterized by a single broad band in the dinitrogen stretching vibrational region at 2135 cm^{-1} and a single broad band in the UV-VIS spectrum

Table 1 Assignment of band positions (in cm^{-1}) of samarium atom absorptions in various matrices at 10 K by comparison with the gas-phase spectrum [13] (relative intensities in brackets).

Gas-phase	CH_4	Ar	Kr	N_2
		29833		29762
		27093		
		26889		
		26738		
		26666	26810	26860
26281 (0.33)	26745	26385	26666	26441
	26178		26385	
			26171	
			26109	
23630 (0.06)	23381	24272	23579	23697
			23469	
		23861		
		23596		
	23100	23305	23315	23299
22914 (0.48)	22889[a]	23213[a]	23047	23073
			22862	
		22994		
		22878		
		22826		
		22732		
		22584		
		22447	22467	
22314 (0.12)	22376	22376[a]	22272	22619
		22080		
		21920		
	21505	21872	21786	
	21427[a]	21701	21561	21872
21194 (0.35)	21186[a]	21308[a]	21186	21678
			21097	20881
20091 (0.25)	20005[a]	20117	20000	20060
	19881	19861	19841	19837
			19763	
18986 (0.03)	—	19246	—	19073
18225 (0.08)	17895	17947	17895	18454
		17784		
17770 (0.08)	17762	17627	17671	17944
			17337	
			17250	

[a] Band vanishes upon annealing.

centred at 647 nm. By analogy with the carbon monoxide studies this should be $Sm(N_2)_6$, but clearly extensive further studies are warranted.

By comparison with previous studies we note with surprise that samarium atoms are at least as photomobile in argon matrices as silver[15] and by far more photomobile than chromium or molybdenum atoms.[16] However, in those cases the resultant clusters were strongly bound, Cr_2 and Mo_2 formally even exhibiting sextuple bonds. The embryonic samarium clusters are obviously more loosely bound as demonstrated by the ease of their destruction, or reaction to higher aggregates, upon brief excitation. Preliminary experiments with other lanthanide atoms indicate a rich variety of reactions among those supposedly very similar metals.

We gratefully acknowledge the skilled technical assistance of Mrs. G. Klihm and Mr. K. Kerpen.

References

1 W. J. Evans, *Adv. Organomet. Chem.*, 1985, **24**, 131.
2 H. Schumann and W. Genthe, in *Handbook on the Physics and Chemistry of Rare Earth*, ed. K. A. Gschneider, Jr. and L. Eyring, Elsevier Science Publishers B.V., Amsterdam, 1984, pp. 445–571.
3 *Organometallic Compounds of the Lanthanides, Actinides and Early Transition Metals*, ed. D. J. Cardin, S. A. Cotton, M. Green and J. A. Labinger, Chapman and Hall, 1985.
4 G. Xu, K. Ren, C. Huang and J. Wu, *Pure Appl. Chem.*, 1988, **60**, 1145.
5 V. V. Zagorsky and G. B. Sergeev, *Mol. Cryst. Liq. Cryst.*, 1990, **186**, 81.
6 H. Imamura, K. Kitajima and S. Tsuchiya, *J. Chem. Soc., Faraday Trans.*, 1989, 1647.
7 K. J. Klabunde, *Chemistry of Free Atoms and Particles*, Academic Press, New York, 1980, ch. 10.
8 W. E. Klotzbücher, *Ph. D. Thesis*, University of Toronto, 1979.
9 W. E. Klotzbücher, *Cryogenics*, 1983, **23**, 554.
10 W. E. Klotzbücher, *J. Mol. Struct.*, 1988, **174**, 5.
11 W. E. Klotzbücher and G. A. Ozin, *Inorg. Chem.*, 1980, **19**, 3767.
12 M. Jacob, H. Micklitz and K. Luchner, *Ber. Bunsenges. Phys. Chem.*, 1978, **82**, 32. The authors report solely on phonon sidebands in the $^7D_1$ transition in the 26800–27200 cm^{-1} region, which we do not observe.
13 D. H. Carstens, W. Brashear, D. R. Eslinger and D. M. Gruen, *Appl. Spectrosc.*, 1972, **26**, 184.
14 I. P. Beletskaya, G. Z. Suleimanov, R. R. Shifrina, R. Yu. Mekhdiev, T. A. Agdamskii, V. N. Khandozhko and N. E. Kolobova, *J. Organomet Chem.*, 1986, **299**, 239.
15 G. A. Ozin and W. E. Klotzbücher, *Inorg. Chem.*, 1979, **18**, 2101.
16 W. E. Klotzbücher and G. A. Ozin, *J. Am. Chem. Soc.*, 1978, **100**, 2262.

Received: Cambridge, 28th September 1993
Moscow, 20th October 1993; Com. 3/05849B