TABLE I

THE EXPLOSIVE PROPERTIES[e] OF SOME METAL AMMINES

Metal ammine[d]	Explosion temperature, °C.[c]	Impact sensitivity 2 kg. wt., cm.	Sand test-gm.			
			Power Sand crushed	Sensitivity to initiator, gm., required to cause complete explosion Mercury fulminate	Lead azide	Tetryl
Hexammine chromium(III) nitrate	265	32	40.7	0.20	..	..
Hexammine cobalt(III) perchlorate	360	18	39.2	.25	..	..
Hexammine cobalt(III) iodate	355	100	14.7	.24	..	..
Hexammine cobalt(III) nitrate	295	50	35.9	.27	..	..
Hexammine cobalt(III) hexanitrocobaltate[a]	...	85	34.0	.20	..	..
Nitratopentammine cobalt(III) nitrate	310	48	35.5	.24	..	..
Chloropentammine cobalt(III) perchlorate	320	21	30.6	.20	..	..
Hexaurea chromium nitrate	265	50	3.0	..	..	..
Thiocyanatopentammine cobalt(III) perchlorate	325	55	20.1	..	..	
Dithiocyanatotetrammine cobalt(III) perchlorate	335	35	13.9	..	..	.
Dichlorodiethylenediamine cobalt(III) perchlorate	300	85	9.9	..	..	..
Dichlorodiethylenediamine cobalt(III) chlorate	320	...	13.7	..	..	..[b]
Trinitrotriammine cobalt(III)	305	44	None	..	..	..
tris-Ethylenediamine cobalt(III) nitrate	...	61	None	..	..	0.4
bis-Diethylenetriamine cobalt(III) perchlorate	325	21	39.4	..	0.07	..
Ammonium hexanitrocobaltate(III)	230	33	19.0	.30	..	..
Tetrammine copper(II) nitrate	330	19	17.2	..	..	0.19
Mercuric fulminate	...	5	21.0	..	..	..
Lead azide	335	10	18.0	..	..	..
TNT (*sym*-trinitrotoluene)	470	95	42.0	.24	..	..

[a] This compound was unstable. [b] Requires tetryl. [c] Exposure to the temperature cited causes very rapid decomposition, or explosion, in 5 seconds. [d] All oxalates, chromates, carbonates, sulfates, and non-oxygenated complexes tested were non-explosive (*e. g.*, hexammine cobalt(III) chromate, oxalate and chloride). No compounds containing explosive groupings (*e. g.*, azide) were tested. [e] For details of tests see Picatinny Arsenal Technical Report No. 1401, 18 March 1944; Bureau of Mines Technical Bulletin No. 346, "Physical Testing of Explosives" at the Bureau of Mines Explosives Experiment Station, Bruceton, Pa.

to be explosive include: hexammine cobalt(III) chlorite,[4] chlorate,[3] and perchlorate,[3,5] aquopentammine cobalt(III) chlorate and perchlorate,[5] trihydrazine cobalt(II) nitrate,[6] hexahydroxylamine cobalt(III) nitrate,[7] the tetrammineauric halides[8] and trinitrotriammine cobalt.[9] In light of the evidence available in literature, it seems quite probable that the explosions reported to have occurred during evaporation of filtrates from cobalt determinations were caused, as suggested by Broughton, Laing and Wentworth,[10] by the formation of complex nitro- or nitro-cobaltates(III).

Samples of a number of cobalt(III) and chromium(III) coördination compounds[11] were subjected to standard tests to determine explosion temperature, impact sensitivity, power and sensitivity to initiation (ease with which explosion can be effected). Results of these tests are compared in Table I with values for TNT, mercuric fulminate and lead azide, representing respectively a relatively insensitive high explosive and two very sensitive initiating agents.

The data show quite clearly that oxygenated coördination compounds, particularly those which are "oxygen balanced," vary quite widely with respect to their sensitivities to heat and impact. They represent an extremely wide range in explosive types. Since most of the compounds are capable of exploding sharply and powerfully, and in some cases with but slight provocation, they are to be considered exceedingly dangerous. Some possess sufficient sensitivity to propagate explosion under water; the use or presence of non-solvent liquids is therefore no guarantee of safety. In the absence of specific information the same considerations may be expected to apply also to other metal ammines containing oxidizing radicals such as those of silver, gold, cadmium, lead and zinc.

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Preparation of Radioactive CO_2 from $BaCO_3$[1]

BY NORMAN ZWIEBEL,[2] JOHN TURKEVICH AND WARREN W. MILLER

To obtain the C^*O_2 from BaC^*O_3 either for introduction into a reaction system for synthesis of a

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(4) Levi, *Atti Lincei*, (5) **32**, I, 623 (1923).

(5) Salvadori, *Gazz. chim. ital.*, **40**, II, 17 (1910).

(6) Franzen and Meyer, *Z. anorg. Chem.*, **60**, 247, 274 (1908).

(7) Werner and Berl, *Ber.*, **38**, 897 (1905).

(8) Ephraim, "Inorganic Chemistry," 4 Ed., Nordeman Publishing Co., Inc., New York, N. Y., 1943, p. 311.

(9) Clark, Quick and Harkins, THIS JOURNAL, **42**, 2498 (1920).

(10) Broughton, Laing and Wentworth, *Anal. Chem.*, **19**, 72 (1947).

(11) The authors desire to acknowledge their indebtedness to Professor John C. Bailar, Jr., of the University of Illinois, for his help in furnishing many of the coördination compounds which were subjected to actual study or used for the preparation of related derivatives.

(1) Work done at the Brookhaven National Laboratory under the auspices of the Atomic Energy Commission. The work was started by one of us (W. W. M.) while a member of the Laboratory of Nuclear Science, Massachusetts Institute of Technology.

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labeled compound, or for transfer to a gas activity measuring device such as an ionization chamber or gas counter, it has been common practice to drop either concentrated phosphoric or sulfuric acid on the $BaCO_3$.[3] This procedure often involves the use of a stopcock in contact with concentrated acid, does not permit the ready attainment of high vacuum and may entail the formation of a crust of insoluble barium sulfate or phosphate around the active barium carbonate. In practice a still more disconcerting factor has been the spattering of the dry powder on contact with acid with the consequent sweeping of a portion of the sample out of the reaction vessel by the evolving gas. The direct thermal evolution of the C^*O_2 from BaC^*O_3 by roasting the dry salt in a quartz tube has also been used[4] but the temperature necessary is inconveniently high.

These difficulties may be surmounted by using a thermal reaction between dry solids to evolve the carbon dioxide. Acids such as potassium bisulfate are unsuitable as the reaction will produce water as well as carbon dioxide. Inorganic acid anhydrides such as boric oxide and the pyro salts melt at too high a temperature to be used in Pyrex apparatus. Organic anhydrides sublime under vacuum. A convenient reaction, however, is a metathetic one producing a thermally unstable carbonate such as the reaction between barium carbonate and lead chloride. Lead chloride was used because it can be readily obtained in an anhydrous state, and has a low melting point and vapor pressure. Silver chloride can also be used.

To obtain the total carbon dioxide from a barium carbonate sample, two procedures have been worked out. In the micro-procedure the weighed barium carbonate, from 5 to 200 mg., is dropped into a Pyrex test-tube with attached ground joint. Over this is layered 5 to 10 times its weight of dry powdered lead chloride, and then a wad of glass wool is pushed down on top. After attaching the tube to the vacuum system and pumping at 100°, the carbon dioxide is released by carefully melting the lead chloride with a micro burner. The reaction is known to be at least 98% complete from gas buret and activity measurements. The fusion temperature may be lowered by using a 50–50 mixture of $PbCl_2$–$AgCl$ instead of pure lead chloride. The melt should not fill a full diameter of the reaction vessel or the latter may crack on cooling. For macro-quantities we have employed the following procedure. The two solids, one part by weight of barium carbonate and six parts by weight of lead chloride, were intimately mixed and ground together before placing the mixture in a reaction tube. The latter was connected to a standard vacuum system by means of a stopcock and a standard taper ground glass joint. The reaction mixture was pumped overnight at room temperature to a pressure of 10^{-5} mm. A tubular woven glass heating mantle was used as a heat source and the temperature was controlled by a Variac. Evolution of gas began at about 180° and each increment of temperature caused a more rapid evolution of gas which gradually decreased with time. It was found that the most convenient procedure was to raise the temperature to 400° as rapidly as possible (about twenty-five minutes) and maintain the reaction mixture at this temperature. The evolution of carbon dioxide was 65% complete in one hour from the start of heating, 80% in two hours and 96% complete in four hours. 3–9 g. of barium carbonate was employed in these experiments. Thus this reaction has been found to proceed at temperatures well below the fusion temperature and the system may therefore be used as a convenient, clean, "virtual" source of active carbon dioxide.

BROOKHAVEN NATIONAL LABORATORY
UPTON, NEW YORK
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[3] (a) W. G. Dauben, J. C. Reid and P. E. Yankwich, *Ind. Eng. Chem., Anal. Ed.*, **19**, 828 (1947); (b) J. T. Kummer, THIS JOURNAL, **69**, 2239 (1947); (c) J. L. Huston and T. H. Norris, *ibid.*, **70**, 1968 (1948).

[4] M. G. Inghram, Atomic Energy Commission, MDDC 60, June, 1946.

COMMUNICATIONS TO THE EDITOR

METALLIC ALUMINUM IN SOLUTION IN LIQUID AMMONIA

Sir:

It has long been generally accepted that the alkali metals, in dissolving in liquid ammonia, dissociate into alkali metal cations and free (solvated) electrons,[1] and that the latter impart the characteristic blue color to such solutions. The alkaline earth metals are known to dissolve similarly, although to a smaller extent.[2] Makishima[3] included the dissolution of electrons among electrode reactions which may occur at a cathode in liquid ammonia solutions, and Laitinen and Nyman[4] have very recently pointed out that, theoretically, all metals should be in some degree soluble in liquid ammonia. According to the hypothesis

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[1] Kraus. THIS JOURNAL. **30**, 1323 (1908).

[2] Kraus, *ibid.*, **30**, 660 (1908).

[3] Makishima, *J. Faculty Eng. Tokyo Imp. Univ.*, **21**, No. 3, 115 (1938).

[4] Laitinen and Nyman, THIS JOURNAL, **70**, 3002 (1948).